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## FREE RADICAL MECHANISMS FOR INHIBITED ORGANIC DECOMPOSITIONS<sup>1</sup>

B. W. WOJCIECHOWSKI AND K. J. LAIDLER

### ABSTRACT

It is suggested that organic decompositions that are fully inhibited by substances such as nitric oxide and propylene proceed not by molecular mechanisms, but by special types of free radical mechanisms in which the inhibitor is involved in both initiation and termination. In the case of nitric oxide inhibition, initiation is considered to be by the abstraction of a hydrogen atom by NO, while termination involves reaction between the most plentiful chain carrier and either HNO or NO, depending upon whether or not H is a chain carrier. Specific mechanisms are proposed for the decompositions of paraffins, ethers, and aldehydes, when inhibited by nitric oxide, and the resulting rate equations are shown to be consistent with the behavior observed experimentally. It is shown for the ethane decomposition that the same limiting rate is obtained for any inhibitor that can become involved in the same type of mechanism.

### INTRODUCTION

In spite of the very considerable amount of work that has been done on the inhibition, by substances such as nitric oxide and propylene, of gaseous organic decompositions, the nature of the mechanisms still remains something of a problem. Certain of the evidence,\* such as that, in many cases, the inhibition leads to constant limiting rates and that the same limiting rates are given by different inhibitors, appears to point to the conclusion that the reactions are molecular in nature. This position has in fact been taken by Hinshelwood and his co-workers, and Stubbs and Hinshelwood (2, 3) have reviewed the evidence leading to this conclusion. On the other hand, there are certain characteristics of the fully inhibited reactions that seem to be incompatible with the view that a purely molecular mechanism is involved. These are in brief as follows:

(1) It has been found by Voevodsky and Poltorak (4) and by Rice and co-workers (5, 6) that hydrogen-deuterium mixing reactions take place as rapidly (relative to the decomposition rates) in certain fully inhibited reactions as they do in the uninhibited reactions.

(2) The fully inhibited reactions frequently exhibit a well-defined induction period, during which the pressure-time curves are S-shaped (7).

(3) The rates of the fully inhibited reactions are sometimes *decreased* by increasing the surface:volume ratio (8).

It would seem to be quite impossible to reconcile these facts with the hypothesis of a simple molecular mechanism, and it is therefore necessary to develop mechanisms of the free radical type that will give rise to limiting rates at high inhibitor concentrations, and will explain the fact that different inhibitors give the same limiting rates.

A suggestion to avoid these difficulties has recently been put forward by Voevodsky

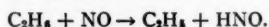
<sup>1</sup>Manuscript received February 25, 1960.

Contribution from the Department of Chemistry, University of Ottawa, Ottawa, Canada.

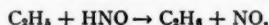
\*The main experimental results referred to in this paper are reviewed in Steacie's book (1).

(9), who has interpreted the fully inhibited decompositions of paraffin hydrocarbons in terms of the idea that initiation and termination both take place on the surface of the vessel. It is proposed by Voevodsky that the initiation reactions are caused by irreversible and reversible surface processes, of which the former can be suppressed by the inhibitors. Full inhibition corresponds to complete coverage of the active centers on the wall. Voevodsky proposes no specific mechanisms, and his suggestion is subject to one serious difficulty: the amount of nitric oxide required to give complete inhibition should depend on the surface:volume ratio, and this is certainly not the case. Also, the S-shaped pressure-time curves, implying abnormally small initial rates, seem inconsistent with Voevodsky's suggestion.

The object of the present paper is to propose specific free radical mechanisms, involving the participation of inhibitor molecules, that appear to be consistent with all of the facts. The essence of our proposals is that in the presence of inhibitors the main initiating processes are hydrogen-abstraction reactions such as



Chain termination is suggested as sometimes involving reactions such as

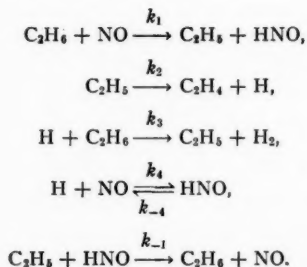


but when hydrogen atoms are not the chain carriers chain termination is regarded as involving NO rather than HNO. Specific reaction mechanisms will be proposed for various types of reactions, including hydrocarbon decompositions and the decompositions of aldehydes and ethers. Additional experimental support for our proposals is being obtained, and the details will be published later.

#### THE DECOMPOSITION OF ETHANE

The thermal decomposition of ethane is a typical example of the decomposition of a paraffin hydrocarbon; the mechanism proposed for this case can readily be modified for the higher paraffins.

The mechanism proposed is



This scheme leads to the following expression for the rate

$$[1] \quad v = (k_1 k_2 k_3 k_{-4} / k_{-1} k_4)^{1/2} [\text{C}_2\text{H}_6].$$

The mechanism is seen to lead to first-order kinetics, as found experimentally (7, 10, 11, 12, 13).

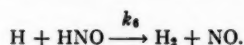
Several comments may be made about this mechanism. Our estimate of the dissociation energy of HNO into  $\text{H} + \text{NO}$  is 44 kcal and this leads to an activation energy of 56 kcal for the initial reaction. The over-all activation energy is then found to be approximately

$$[2] \quad E = \frac{1}{2}(E_1 + E_2 + E_3 + E_{-4} - E_{-1} - E_4),$$

$$[3] \quad = \frac{1}{2}(56 + 40 + 10 + 44 - 0 - 0) = 75 \text{ kcal},$$

which is close to the experimental value (74–77 kcal). Using these values it is found that with about 10% of nitric oxide the rate of the initiation reaction is appreciably greater than that of the splitting of ethane into two methyl radicals, so that in the presence of excess nitric oxide the latter reaction may be neglected. The fully inhibited reaction therefore occurs largely by the mechanism proposed above, and the rate is seen to be independent of the nitric oxide concentration. At lower concentrations of nitric oxide the two mechanisms occur at comparable rates and inhibition is only partial. The steady-state equation then involves the solution of a cubic equation, and a simple expression for the rate of the partially inhibited reaction cannot be obtained.

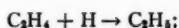
As will be discussed in more detail in a separate paper (13), the NO-inhibited decomposition of ethane has an S-shaped pressure-time curve. The initial rates are found to exhibit 3/2-order kinetics, and this can be explained by taking the chain-ending step to be



The rate equation is now

$$[4] \quad v = k_3(k_1k_{-4}/k_4k_6)^{1/2}[\text{C}_2\text{H}_6]^{3/2}.$$

In general, termination involving reaction between HNO and a  $\mu$  radical (one undergoing first-order reactions) leads to first-order kinetics, while the reaction of HNO with a  $\beta$  radical (one undergoing second-order reactions) leads to kinetics of order 3/2. At the very beginning of the inhibited reaction H atoms are more plentiful than  $\text{C}_2\text{H}_5$  radicals, but as small amounts of ethylene accumulate this situation is reversed as a result of the reaction



the main chain-ending step, therefore, changes in the manner indicated.

When the ethane decomposition is partially inhibited by nitric oxide the degree of inhibition is found to be less at higher ethane concentrations (10, 11). This effect is attributed to the fact that nitric oxide competes with ethane for hydrogen atoms. It is significant that this effect is not found with the ethers for which, as discussed below, chain termination is believed to involve NO and not HNO.

The fact that propylene and other inhibitors inhibit to exactly the same limiting extent as NO is readily explained in terms of equation [1]. It is postulated that in propylene inhibition the allyl radicals (produced in the decomposition of propylene) play the same role as NO and initiate chains according to the reaction



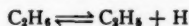
Propylene itself plays the same role as HNO, and terminates by the reaction



In equation [1] the rate constants involving the inhibitor are  $k_1$ ,  $k_{-1}$ ,  $k_4$ , and  $k_{-4}$ , and they appear in the ratio

$$k_1/k_{-1} \cdot k_{-4}/k_4.$$

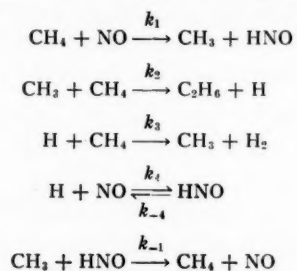
This ratio is the equilibrium constant for the reaction



and since this reaction does not involve the inhibitor the limiting rate will be the same for all inhibitors capable of inhibiting by this type of mechanism. The result that more propylene is required to give the same inhibition as produced by NO is attributed to the fact that NO is more plentiful than allyl radicals.

#### THE DECOMPOSITION OF METHANE

The decomposition of methane offers an interesting contrast to that of ethane, since both of the chain-propagating reactions are of the second order. The chain carriers are H and CH<sub>3</sub>, and one obtains 3/2-order kinetics whether one assumes the chain termination to involve CH<sub>3</sub> + HNO or H + HNO. The former is preferred since the methyl radical concentration is probably usually higher than the concentration of hydrogen atoms. The mechanism to which we are therefore led is as follows:



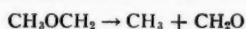
The expression for the limiting rate is

$$[5] \quad v = (k_1 k_2 k_3 k_{-4} / k_{-1} k_4)^{1/2} [\text{CH}_4]^{3/2}.$$

The conclusion that the order is 3/2 is consistent with the experimental results (11).

#### THE DECOMPOSITION OF ETHERS

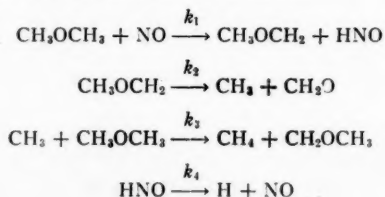
In the reactions discussed above hydrogen atoms were involved in chain-propagating steps. In ether decompositions, on the other hand, this is not the case; the chain-propagating reactions in the case of dimethyl ether are probably



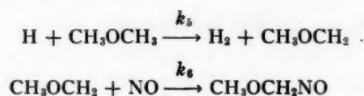
and



In view of this the concentration of HNO is very small, and the participation of HNO in chain termination is therefore unlikely. Our suggestion is that in these reactions chain termination involves nitric oxide itself, reacting with whichever radical is present in greater concentration; in the ether decomposition these are the  $\mu$  radicals. The mechanism to which we are led is therefore as follows:





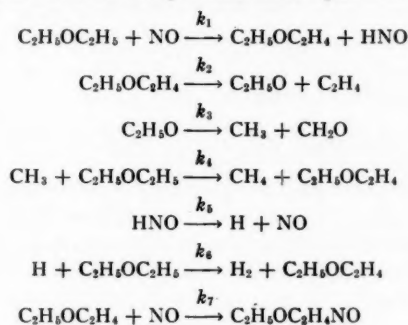


Application of the steady-state treatment gives rise to the rate equation

$$[6] \quad v = (2k_1k_2/k_6)[\text{CH}_3\text{OCH}_3].$$

The result that the reaction is of the first order is in general agreement with experiment, although some complications certainly exist (14, 15).

The proposed mechanism for the diethyl ether decomposition is similar, as follows:



The rate equation is now

$$[7] \quad v = (2k_1k_2/k_7)[\text{C}_2\text{H}_5\text{OC}_2\text{H}_5]$$

and the order is again the first, as found experimentally (16).

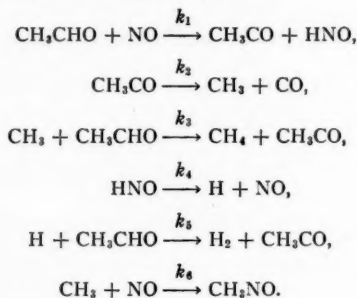
It is significant that in these ether decompositions the nitric oxide is in no way in competition with the ether molecules themselves. The nitric oxide reacts with a  $\mu$  radical, and the situation is to be contrasted with that in the case of ethane where nitric oxide competes with  $\text{C}_2\text{H}_6$  for reaction with hydrogen atoms. In the ether decompositions the degree of inhibition produced by a given nitric oxide concentration is thus independent of the amount of ether, a prediction that is consistent with experiment.

In contrast to the situation with methane and ethane (and by analogy with the higher paraffins), the mechanism proposed for the ethers does not lead to the general conclusion that the fully inhibited rate should be the same for all inhibitors. Smith and Hinshelwood (16) and Freeman (15) have obtained results that tend to show that the same rates are obtained with both nitric oxide and propylene and this being so it must be assumed, if our mechanisms are correct, that the agreement of rates is fortuitous. It should, however, be pointed out that in the case of the ether decompositions there does remain a possibility that the fully inhibited reactions are molecular processes, since no isotopic exchange experiments have been carried out on these reactions.

#### THE DECOMPOSITION OF ACETALDEHYDE

The acetaldehyde decomposition differs from the hydrocarbon decompositions, and is similar to the ether decompositions in that hydrogen atoms are not chain carriers. Chain termination will therefore involve NO rather than HNO. The chain carriers are  $\text{CH}_3$  and  $\text{CH}_3\text{CO}$ , of which the former are in excess; it is therefore postulated that the chain-ending step is reaction between  $\text{CH}_3$  (a  $\beta$  radical) and NO.

The mechanism to which we are led is therefore:



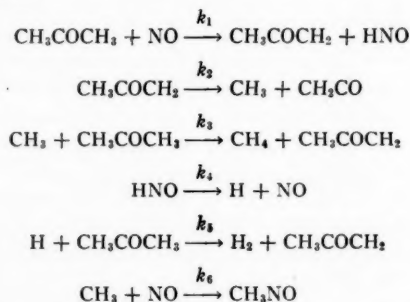
The rate corresponding to this mechanism is

$$[8] \quad v = (2k_1k_3/k_6)[\text{CH}_3\text{CHO}]^2 + 2k_1[\text{CH}_3\text{CHO}][\text{NO}].$$

This rate expression, as in previous cases, corresponds to the rate when there is a sufficient excess of nitric oxide: much more complicated expressions result if the uninhibited initiation step is included also. The mechanism in this case leads to initial inhibition, with acceleration at higher nitric oxide concentrations as the second term in the rate equation becomes predominant. This is in fact the behavior observed experimentally (16). At moderate concentrations of nitric oxide the first term will predominate, and the kinetics should therefore be of the second order, as is found experimentally (16).

#### THE DECOMPOSITION OF ACETONE

The nitric oxide inhibited decomposition of acetone is very similar to that of acetaldehyde (there is again catalysis at high concentrations) and a similar mechanism is therefore probably involved.



The resulting rate expression is

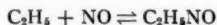
$$[9] \quad v = (2k_1k_3/k_6)[\text{CH}_3\text{COCH}_3]^2 + 2k_1[\text{CH}_3\text{COCH}_3][\text{NO}],$$

which is consistent with experiment (17).

The fact that the proposed mechanisms for these last two examples lead to the conclusion that there is catalysis at high nitric oxide concentrations, as observed experimentally, provides valuable support for the general scheme of reactions proposed in this paper.

## GENERAL DISCUSSION

The suggestion that the initiating processes in reactions fully inhibited by nitric oxide involve a hydrogen atom abstraction by NO is not new; it was first made by Rice and Polly (18) and was discussed by Goldanskii (19). However, the postulation of reactions between radicals and HNO as chain-terminating steps appears to be new,\* and seems to be required in order to account for the observed kinetics, and more particularly to explain the cases of limiting rates at high nitric oxide concentrations. Our view is that in the paraffin decompositions, where rather high temperatures are involved, reactions such as



merely proceed to equilibrium and do not disturb the steady-state concentrations of radicals; they therefore need not be included in the reaction schemes. In reactions at lower temperatures, however, such reactions are important chain-ending steps.

The idea that the radical HNO plays an important role in reaction mechanisms is reasonable in view of the fact that this substance has been prepared and its spectrum analyzed (21). Since the molecule is isoelectronic with O<sub>2</sub> it may be expected to be quite stable with respect to H + NO.

The reaction mechanisms discussed above may be seen to fall into four main classes, and Table I summarizes the main features and gives examples of each type.

TABLE I  
Summary of reaction types for inhibition by nitric oxide

Case	H as chain carrier	Chain-ending step	Order of reaction	Examples	Chain carriers (most abundant given first)	Chain-ending step
I	Yes	$\mu + HNO$	1	$C_2H_6$	$C_2H_5$ , H	$C_2H_5 + HNO$
II	Yes	$\beta + HNO$	3/2	$C_2H_6$ (initial rates)	H, $C_2H_5$	$H + HNO$
III	No	$\mu + NO$	1	$CH_4$ $CH_3OCH_3$ $C_2H_5OC_2H_5$	$CH_3$ , H $CH_3OCH_2$ , $CH_3$ $C_2H_5OC_2H_4$ , $CH_3$	$CH_3 + HNO$ $CH_3OCH_2 + NO$ $C_2H_5OC_2H_4 + NO$
IV	No	$\beta + NO$	2	$CH_3CHO$ $CH_3COCH_3$	$CH_3$ , $CH_3CO$ $CH_3$ , $CH_3COCH_2$	$CH_3 + NO$ $CH_3 + NO$

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\*Except for the rather special case of the nitrite decompositions for which Levy (20) includes  $RO + HNO \rightarrow ROH + NO$  as a minor chain-ending step which does not affect the over-all rate expression.

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## THE STRUCTURE AND STEREOISOMERISM OF THREE MITRAGYNA ALKALOIDS<sup>1</sup>

J. C. SEATON,<sup>2</sup> M. D. NAIR,<sup>2</sup> O. E. EDWARDS, AND LÉO MARION

### ABSTRACT

Isorhyncophylline, the isomer into which rhyncophylline is convertible, has been found to occur in nature. Both bases are interconvertible. Isorhyncophylline on hydrolysis with dilute hydrochloric acid is converted to an aldehyde reducible to isorhyncophyllol. When the aldehyde is reduced in the Wolff-Kishner reaction, it is also isomerized and the product is isorhyncophyllane. This reduction product is oxidized by mercuric acetate to a neutral dilactam which still contains the oxindole carbonyl and further contains a new lactam carbonyl present in a six-membered ring. Reduction of the dilactam with lithium aluminum hydride gave a product having the spectroscopic properties of an indole. This confirms the assumption previously made that in rhyncophylline, ring C is five-membered. The isomerization of rhyncophylline, mitraphylline, and formosanine is described. Formosanine has been shown to be identical with uncarine-B and thus uncarine-A is the iso base derivable from formosanine.

It has been reported first by Kondo, Fukuda, and Tomita (1) that rhyncophylline in acetic acid isomerizes to isorhyncophylline. It has now been possible to isolate isorhyncophylline from *Adina rubrostipulata* K. Schuman. It separated from the mother liquors that had already yielded rhyncophylline and mitraphylline. It was isolated as the perchlorate from which the crystalline base was liberated. Its ultraviolet spectrum was identical with that of rhyncophylline, and the infrared spectra of the two bases were very similar so that the isomerization did not seem to involve the chromophoric groups. When either rhyncophylline or its isomer was refluxed in pyridine it was converted to a mixture consisting of 30% rhyncophylline - 70% isorhyncophylline.

Whereas on catalytic hydrogenation rhyncophylline is converted to hexahydro-rhyncophylline, in which the enol-ether double bond has survived, the similar hydrogenation of isorhyncophylline converts it to octahydroisorhyncophylline. The ultraviolet spectrum of this product showed only end absorption while the infrared spectrum contained absorption bands due to an unconjugated ester group ( $1743\text{ cm}^{-1}$ ) and an oxindole carbonyl ( $1700\text{ cm}^{-1}$ ) although it contained no absorption attributable to a benzene ring or an enol ether.

Hydrolysis of isorhyncophylline with dilute hydrochloric acid yielded a product having the properties of an aldehyde (a precipitate with Brady's reagent and restoration of color to Schiff's reagent), but it was not possible to induce the base or a salt to crystallize. The base appeared to polymerize on standing for a short time.

Reduction of the crude product, however, with sodium borohydride gave a base isomeric with rhyncophyllol (2), i.e., isorhyncophyllol ( $\text{C}_{19}\text{H}_{26}\text{O}_2\text{N}_2$ ), the picrate of which crystallized. The regenerated base was a glass and its infrared spectrum in chloroform showed bands at  $3610\text{ cm}^{-1}$  (hydroxyl),  $3425\text{ cm}^{-1}$  (imino group),  $1717\text{ cm}^{-1}$  (oxindole carbonyl), and  $1628\text{ cm}^{-1}$  (benzene ring).

The amorphous aldehydic product of the hydrolysis of isorhyncophylline (i.e. isorhyncophyllal) when subjected to the Wolff-Kishner reaction suffered reduction of its aldehyde group. The product (73% yield) was identical with rhyncophyllane ( $\text{C}_{19}\text{H}_{26}\text{ON}_2$ ) obtained previously (2) from rhyncophylline by the same reactions. In view of the fact that the thermal rearrangement of rhyncophylline and of rhyncophyllol gives mixtures in which

<sup>1</sup>Manuscript received January 28, 1960.

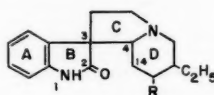
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<sup>2</sup>National Research Council of Canada Postdoctorate Fellow.

the isobase always predominates, it is more likely that this common product is isorhyncophyllane. Consequently, rhyncophyllane would have been more correctly named isorhyncophyllane, and we propose to adopt the latter designation.

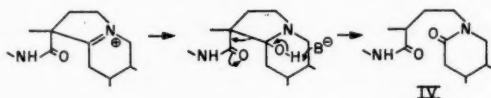
The structure of rhyncophylline represented by formula I has been suggested previously (2). From the foregoing results isorhyncophylline must also be represented by formula I



- I,  $R = \text{CH}_2\text{OOC}-\text{C}=\text{CH}.\text{OCH}_3$   
 II,  $R = -\text{CH}_2.\text{CH}_2\text{OH}$   
 III,  $R = .\text{CH}_2\text{CH}_3$

although the stereochemistry of the bases is different while isorhyncophyllol must be II and isorhyncophyllane III. Methylation with sodium methoxide converted isorhyncophyllane to N-methylisorhyncophyllane, which was crystallized as its picrate, m.p. 182–184°.

The final evidence needed to complete the proof that rhyncophylline (2) and its stereoisomer isorhyncophylline have structure I was the point of linkage of C-3 to ring D, and this has now been provided. Isorhyncophyllane reacted quickly with 1 mole of mercuric acetate giving rise to a neutral dilactam which in the infrared showed bands at  $1715\text{ cm}^{-1}$  (oxindole carbonyl) and at  $1625\text{ cm}^{-1}$  (six-membered lactam). This dilactam could not be crystallized, nor could it be purified completely because of partial decomposition when it was dissolved in a hot solvent. Lithium aluminum hydride in refluxing dioxane reduced the dilactam to a sensitive base which could not be purified without decomposition, but had an infrared spectrum showing no carbonyl absorption and an ultraviolet spectrum similar to an indole spectrum. The indication of indole formation on reduction, although not rigorous, does show, if taken in conjunction with the formation of a lactam in the reaction with mercuric acetate, the location of the new carbonyl. Thus the evidence is consistent with structure IV for the dilactam which must have been produced via the immonium ion and

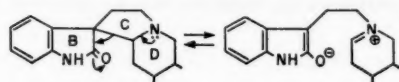


carbinolamine as shown. It further establishes the five-membered nature of ring C.

Perhaps the most intriguing feature of rhyncophylline chemistry is the isomerization to isorhyncophylline. That the enol-ether system was not involved was shown by the fact that rhyncophyllol isomerizes in identical manner. Nozoye (3, 4) has suggested that the isomerism involves the configuration at C-4. A more plausible explanation of this phenomenon seemed to us to be the following thermal (possibly also acid-catalyzed) fission-recoupling process,<sup>5</sup> which involves the two asymmetric centers C-3 and C-4.

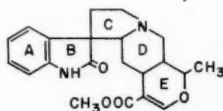
The pair of structures which represent rhyncophylline and its isomer must satisfy the requirements that the equilibrium between the two lies 70% on the side of the iso series,

<sup>5</sup>This mechanism was recently independently suggested by Wenkert, Udelhofen, and Bhattacharyya (5).



that rhyncophylline and derivatives are inert to mercuric acetate while the iso series react rapidly, and that the rhyncophylline series are stronger bases than the iso series. A rigorous assignment of stereochemical structures is not yet possible.<sup>4</sup>

An equilibrium mixture of 20% mitraphylline and 80% isomitraphylline is formed when either base is refluxed in pyridine overnight. It has not been possible to obtain isomitraphylline crystalline, but its picrate was a well-defined compound and the analytical figures obtained for this salt corresponded to  $C_{21}H_{24}O_4N_2$  for the base. The ultraviolet spectrum of isomitraphylline was almost identical with that of mitraphylline (6) and the infrared spectra of the two bases showed no significant shift in the frequencies of the bands corresponding to the functional groups. Isomitraphylline when oxidized with mercuric acetate gave an amorphous product which on hydrogenation over Adams' catalyst produced a mixture of isomitraphylline and mitraphylline. The isomerism parallels that of rhyncophylline. Mitraphylline has been shown (6) to possess structure V, which must also represent isomitraphylline.



V

The alkaloid formosanine was isolated from *Orouparia formosana* Mats by Raymond-Hamet (7). It has the formula  $C_{21}H_{24}O_4N_2$  and contains one methoxyl group. It has been suggested by Loudon (8) and by Raymond-Hamet (9) that uncarine-B isolated by Kondo (10) from *Uncaria kawakamii* Hayata was identical with formosanine because their melting points, rotations, and ultraviolet spectra were almost identical. We have now been able to make a direct comparison of formosanine<sup>5</sup> with a sample of uncarine-B kindly supplied by Professor H. Kondo. The melting point of the mixture of the bases showed no depression and their X-ray powder diagrams were identical while their infrared absorption spectra were virtually identical. This confirms the claim of Raymond-Hamet (9) that formosanine and uncarine-B are identical.

The pair of alkaloids uncarine-A-uncarine-B (formosanine) have been assigned structure V (3), which is also that of mitraphylline (6). When boiled with pyridine, formosanine is equilibrated to a mixture of about 20% formosanine and 80% isoformosanine. Formosanine is isomeric with mitraphylline, but not identical with it. Whereas mitraphylline was hydrogenated catalytically to hexahydromitraphylline in which the

<sup>4</sup>An analysis of the stereochemistry is possible, and leads to a conclusion respecting the structures of the two isomers. This speculation, however, is based on rather arbitrary assumptions which will require further experimental confirmation.

<sup>5</sup>Dr. Raymond-Hamet kindly gave us a generous sample of formosanine and we acknowledge our indebtedness and gratitude.

isolated double bond was still present, catalytic hydrogenation converted formosanine to octahydroformosanine.

The three alkaloids rhyncophylline, mitraphylline, and formosanine have a very low solubility in ether, and crystallize readily, while the bases of the iso series are very soluble in ether and either crystallize with difficulty or not at all. The bases equilibrate under the same conditions and in the mixtures produced, the iso base always predominates. Furthermore, the normal series are stronger bases than the iso series. It is therefore most probable that the isomerization in each case is of the same type.

It has been shown (3) that formosanine (uncarine-B) possesses the same structure V as mitraphylline, and also that uncarine-A (isoformosanine) is different from isomitraphylline or its isomer. Hence mitraphylline and formosanine must differ by an isomerism other than that differentiating mitraphylline from isomitraphylline.

The infrared spectra were measured on a Perkin-Elmer double-beam spectrophotometer model 21. Unless otherwise mentioned the spectra were taken in Nujol mulls, and the absorption bands are reported in wave numbers sometimes followed by a numeral in parentheses indicating the percentage absorption.

#### EXPERIMENTAL

##### *Isolation of Isorhyncophylline*

Both rhyncophylline and mitraphylline have already been reported as occurring in *Adina rubrostipulata* K. Schuman. The mother liquors from which the two bases had separated still contained basic material which was precipitated with picric acid. A sample of the crude picrate was suspended in methanol and shaken with Amberlite IRA 400 (basic form) and the mixture poured on a column of Amberlite IRA 400. Elution with methanol gave a solution of bases which was evaporated to dryness under diminished pressure. The basic residue was dissolved in the minimum volume of methanol and the solution made just acid to Congo red with perchloric acid. About half the solvent was evaporated and water added to incipient turbidity. After cooling and scratching a salt crystallized which was recrystallized from methanol from which it separated as colorless needles, m.p. 158–160°. It did not depress the melting point of an authentic sample of isorhyncophylline perchlorate prepared from rhyncophylline by isomerization. Found: C, 52.84; H, 6.19; N, 5.45. Calc. for  $C_{22}H_{28}O_4N_2 \cdot HClO_4 \cdot H_2O$ : C, 52.53; H, 6.21; N, 5.57%.

To liberate the base, the perchlorate was suspended in aqueous ammonia and the mixture extracted repeatedly with ether. The extract was washed with water, evaporated to dryness, and the residue dissolved in ether-hexane from which it crystallized as colorless fine needles, m.p. 150°. The infrared spectrum of the free base, 3420  $cm^{-1}$  (HN), 1730  $cm^{-1}$  (ester carbonyl), 1705  $cm^{-1}$  (oxindole carbonyl), 1645  $cm^{-1}$  (enol-ether), 1625 and 755  $cm^{-1}$  (benzene ring), was identical with that of isorhyncophylline, and so were the ultraviolet spectra,  $[\alpha]_D^{25} +5.9$  (c, 3.95 in ethanol). Found: C, 68.89; H, 7.40; N, 7.21. Calc. for  $C_{22}H_{28}O_4N_2$ : C, 68.72; H, 7.34; N, 7.29%.

##### *Octahydroisorhyncophylline*

Isorhyncophylline (100 mg) was hydrogenated in glacial acetic acid (10 ml) over Adams' catalyst (100 mg) at 27° and a pressure of 755 mm of mercury. The absorption of hydrogen amounted to 26.7 ml and the volume calculated for four double bonds was 25.8 ml. After removal of the catalyst and solvent the residue was alkalinized with sodium carbonate and the mixture extracted with ether. The extract was dried, the solvent



evaporated, and the residue crystallized in ether from which it separated as colorless prisms, m.p. 169–172°,  $[\alpha]_D^{24} +46.9^\circ$  (*c*, 0.49 in ethanol). Found: C, 67.33; H, 9.14. Calc. for  $C_{22}H_{30}O_4N_2$ : C, 67.31; H, 9.24%. Infrared spectrum: 1745, 1700, and 1110  $cm^{-1}$ . Ultraviolet spectrum: end absorption.

#### *Isomerization of Isorhyncophylline*

Isorhyncophylline (280 mg) was refluxed with acetic anhydride (6 ml) for 3 hours. The solvent was removed under diminished pressure, the residue dissolved in benzene and chromatographed on alumina. Elution with benzene–ether gave a fraction (200 mg) which failed to crystallize, but formed a perchlorate which, after crystallization from methanol–ether, melted at 219–220° identical with isorhyncophylline perchlorate by mixed melting point and comparison of infrared spectra. Further elution with chloroform yielded rhyncophylline, m.p. 209–211° identical with an authentic specimen.

#### *Equilibration of Rhyncophylline and Isorhyncophylline*

Rhyncophylline (342 mg) was refluxed overnight in pyridine (7 ml). The solvent was evaporated off, the residue dissolved in ether, and the solution seeded with rhyncophylline. The crystalline base (96 mg) identified with rhyncophylline by melting point, mixed melting point, and infrared spectrum was filtered and the filtrate made just acid with perchloric acid. The crystalline salt (330 mg) was identical with isorhyncophylline perchlorate. Hence the equilibrium mixture contains approximately 30% rhyncophylline and 70% isorhyncophylline.

#### *Isorhyncophyllol*

It has been shown earlier (2) that rhyncophylline is converted to rhyncophyllal by the action of dilute hydrochloric acid. In an attempt to prepare isorhyncophyllal, isorhyncophylline (1.65 g) was refluxed similarly with 8% hydrochloric acid (200 ml) for 3.5 hours. The cooled solution was neutralized with sodium bicarbonate and extracted with ether. The extract was dried over sodium sulphate and evaporated to dryness. The residual gum was soluble in ether, acetone, benzene, methanol, and ethanol, but much less in hexane. After a short time it became only partially soluble in ether. The product could not be crystallized nor could its picrate and perchlorate. It behaved as an aldehyde in that it gave a precipitate with Brady's reagent and restored the color to Schiff's reagent.

The gummy product of the above reaction (100 mg) was dissolved in 80% methanol (15 ml) and sodium borohydride (1.0 g) was added to the solution. After 2 hours the methanol was evaporated and a little water added to the residue which was extracted with ether. The extract was dried over sodium sulphate and the solvent distilled off. There was left a gum which was converted to a picrate that crystallized from methanol as large yellow prisms (0.8 g), m.p. 168–170°. Found: C, 55.39; H, 5.31. Calc. for  $C_{19}H_{26}O_2N_2 \cdot C_6H_3O_7N_3$ : C, 55.24; H, 5.38%. The base was regenerated from a solution of the picrate in methanol on a basic resin (Amberlite IRA 400). It consisted of a colorless glass which could not be crystallized,  $[\alpha]_D^{22} +41.9^\circ$  (*c*, 0.99 in ethanol). Found: C, 72.73; H, 8.34; N, 8.81. Calc. for  $C_{19}H_{26}O_2N_2$ : C, 72.58; H, 8.34; N, 8.91%.

#### *Isomerization of Rhyncophyllol*

A sample (2) of crystalline rhyncophyllol (100 mg) was refluxed in pyridine (25 ml) overnight. The solvent was then evaporated leaving a gum which failed to crystallize. It was dissolved in methanol and converted to the picrate which separated in yellow prisms (135 mg), m.p. 168–169°, undepressed in admixture with the picrate of isorhyncophyllol obtained by reduction of isorhyncophyllal.

*Wolff-Kishner Reduction of Isorhyncophyllal*

Amorphous isorhyncophyllal (400 mg) was reduced by the Huang-Minlon modification of the Wolff-Kishner reaction. The reaction mixture, after being cooled, was acidified with *N* hydrochloric acid and extracted with ether. The aqueous layer was alkalinized with sodium carbonate and extracted repeatedly with ether. The extract from the basic solution was washed with water, dried over sodium sulphate, and evaporated to dryness. The residual stiff gum (205 mg) was distilled at 200° under 6.3 mm and obtained as a colorless glass which formed a picrate that crystallized from ethanol, m.p. 226–227°, either alone or in admixture with rhyncophyllane picrate (2). Found: C, 56.95; H, 5.26. Calc. for  $C_{19}H_{26}ON_2 \cdot C_6H_3O_7N_3$ : C, 56.92; H, 5.54%. The base, liberated on Amberlite IRA 400, had  $[\alpha]_D^{24} +26.2^\circ$  (*c*, 2.1 in ethanol) and its infrared absorption spectrum was identical with that of rhyncophyllane. As explained above, this compound should be renamed isorhyncophyllane.

*N-Methylisorhyncophyllane*

To a solution of isorhyncophyllane (60 mg) in methanol (5 ml) was added a methanolic solution of sodium methoxide (sodium, 50 mg, in methanol, 5 ml) and methyl iodide (1 ml). The mixture was refluxed on the water bath for 3 hours and then evaporated to dryness. The residue was extracted with ether, the extract washed with water, dried over sodium sulphate, and evaporated. A gummy residue was thus obtained which was dissolved in ethanol and converted to the picrate which separated as yellow prisms (50 mg), m.p. 182–184°. Found: C, 58.12; H, 5.86. Calc. for  $C_{20}H_{28}ON_2 \cdot C_6H_3O_7N_3$ : C, 57.66; H, 5.77%. The base liberated on Amberlite IRA 400 did not show any absorption bands in the NH—OH region of the infrared.

*Mercuric Acetate Oxidation of Isorhyncophyllane*

To a solution of isorhyncophyllane (400 mg) in 5% aqueous acetic acid (5 ml) was added mercuric acetate (2.4 g) dissolved in 5% aqueous acetic acid (10 ml) and the mixture heated on the steam bath. A precipitate of mercurous acetate started to appear after 15 minutes. The mixture was heated for 4 hours, cooled, and filtered. The dried mercurous acetate weighed 687 mg. The filtrate was boiled and treated with hydrogen sulphide until precipitation was complete. The mercuric sulphide was filtered off through supercel and the filtrate alkalinized with excess sodium carbonate and extracted three times with chloroform. The extract was washed first with several portions of dilute hydrochloric acid then with water, dried over sodium sulphate, and evaporated. It left a neutral residue (180 mg) which could not be induced to crystallize and could not be distilled without some decomposition. The infrared spectrum of the product showed in addition to the oxindole carbonyl at  $1705\text{ cm}^{-1}$  a strong band at  $1625\text{ cm}^{-1}$  indicative of a six-membered lactam. Found: C, 70.99; H, 8.20. Calc. for  $C_{19}H_{26}O_2N_2$ : C, 72.58; H, 8.34%.

*Reduction of Oxidation Product*

Reduction of the oxidation product with lithium aluminum hydride in ether, in tetrahydrofuran, and in dioxane was attempted under the usual experimental conditions. Although the six-membered lactam carbonyl was reduced readily, the oxindole carbonyl could not be completely reduced. To a solution of lithium aluminum hydride (150 mg) in dry ether was added a solution of the oxidation product (98 mg) in dioxane (10 ml). The ether was evaporated off and the resulting slurry boiled under reflux for 24 hours under dry nitrogen. After the reaction mixture was cooled, the excess lithium aluminum hydride

was decomposed with water and the solution extracted with chloroform. The extract was washed with water and then with *N* sulphuric acid. The acid solution turned violet. It was made basic with aqueous sodium carbonate and extracted with chloroform. The extract yielded a gum (29 mg) which could not be crystallized and from which no crystalline salt could be obtained. The infrared spectrum of the product still contained a weak oxindole carbonyl band, but the lactam carbonyl absorption had completely disappeared.

#### *Isomitraphylline*

Mitraphylline (325 mg) was refluxed in pyridine (25 ml) overnight. The solvent was evaporated and the residue dissolved in a small volume of ether. After cooling for several hours, mitraphylline, m.p. 265 (66 mg), had crystallized. The residue recovered from the mother liquor was converted into a picrate which crystallized from methanol as yellow prisms, m.p. 223° (dec.) (377 mg). Found: C, 54.31; H, 4.38. Calc. for  $C_{21}H_{24}O_4N_2 \cdot C_6H_3O_7N_3$ : C, 54.36; H, 4.56%. The base, regenerated from the picrate on Amberlite IRA 400 was soluble in ether. It could not be induced to crystallize. Found: C, 68.03; H, 6.60; N, 7.42. Calc. for  $C_{21}H_{24}O_4N_2$ : C, 68.46; H, 6.57; N, 7.60%. Infrared spectrum in chloroform: 3440, 1720(87), 1626(72), 1118(63), 1098(62)  $cm^{-1}$ .

#### *Dehydrogenation of Isomitraphylline and Mitraphylline*

(a) Isomitraphylline (110 mg) and mercuric acetate (400 mg) in 5% acetic acid (4 ml) was kept at 40–50°. Precipitation of mercurous acetate started after 2 minutes. After 7 hours the reaction mixture was worked up as described for isorhynchophylline, and the product was converted to perchlorate. Reduction of the perchlorate in 80% methanol with sodium borohydride produced a mixture which was separated into mitraphylline (2 mg) and isomitraphylline isolated as the picrate (20 mg), m.p. 223–227°, undepressed by admixture with an authentic sample.

(b) When mitraphylline (100 mg) and mercuric acetate in 5% acetic acid were kept at 40–50° for 7 hours, only a trace of mercurous acetate had precipitated.

#### *Octahydroformosanine*

Formosanine (25 mg) was hydrogenated in glacial acetic (10 ml) over Adams' catalyst (50 mg) at 27° and 756 mm. The hydrogen absorbed was 8.1 ml (calculated for four double bonds, 7.2 ml). The catalyst and solvent were removed and the residue alkalinized with sodium carbonate solution and extracted with ether. The extract was dried over sodium sulphate, evaporated to dryness, and the residue crystallized from ether from which it separated as colorless cubes (12.5 mg), m.p. 110–120°. Found: C, 66.74; H, 8.59. Calc. for  $C_{21}H_{32}O_4N_2$ : C, 66.99; H, 8.57%. Infrared spectrum: 1745(80), 1707(92), 1100(81)  $cm^{-1}$ .

#### *Equilibration of Formosanine*

Formosanine (45 mg) was refluxed in pyridine overnight. The solvent was evaporated and the residue dissolved in a small volume of ether from which crystals of formosanine, m.p. 218° (8 mg), were deposited. The fraction more readily soluble in ether did not crystallize (uncarine-A) and was dissolved in carbon disulphide for determination of its infrared spectrum.

#### ACKNOWLEDGMENTS

We acknowledge with thanks the courtesy of Professor H. Kondo for the sample he sent us and Dr. Raymond-Hamet for his generous gift of formosanine. We are also grateful to Mr. R. Lauzon for taking the infrared spectra and to Mr. J. R. H. Seguin for the microanalyses.

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## THE RADIOLYSIS OF CYCLOHEXANE

### II. CYCLOHEXANE-CYCLOHEXENE SOLUTIONS AND PURE CYCLOHEXENE<sup>1</sup>

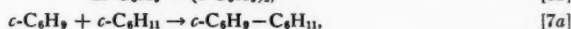
G. R. FREEMAN

#### ABSTRACT

The  $\gamma$ -radiolysis of cyclohexane-cyclohexene solutions and of pure cyclohexene has been investigated. The previously determined yields of the two activated species in irradiated cyclohexane have been confirmed.  $G(c\text{-C}_6\text{H}_{12}'') = 3.0 \pm 0.3$  and  $G(c\text{-C}_6\text{H}_{12}') = 2.4 \pm 0.3$ .

The yields of the main products of cyclohexene radiolysis are  $G(\text{H}_2) = 1.2$ ,  $G(c\text{-C}_6\text{H}_{12}) = 1.0$ ,  $G[(c\text{-C}_6\text{H}_9)_2] = 1.4$ , and  $G(c\text{-C}_6\text{H}_9 \rightarrow \text{higher polymer}) \approx 4$ . There were smaller amounts of ethylene, acetylene, a  $\text{C}_4$  hydrocarbon (probably butadiene), cyclohexylcyclohexene, and dicyclohexyl.

For the reactions



and

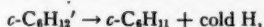


the value  $k_{7a}/(k_{5a}k_{8a})^{1/2} = 0.45 \pm 0.08$  was determined.

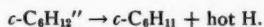
The reaction mechanism that occurs during the radiolysis of cyclohexane-cyclohexene solutions is similar to that which occurs during the radiolysis of cyclohexane-benzene solutions (Part I of this series) with the additional consideration that cyclohexene itself is considerably decomposed during the radiolysis.

#### INTRODUCTION

Two distinct reactive species appear to be important in the  $\gamma$ -radiolysis of cyclohexane (1). One reactive species,  $c\text{-C}_6\text{H}_{12}''$ , is subject to energy transfer "protection" by benzene and the other,  $c\text{-C}_6\text{H}_{12}'$ , is not. It also appears that  $c\text{-C}_6\text{H}_{12}'$  decomposes to produce "cold" hydrogen atoms that can be scavenged by benzene,



whereas  $c\text{-C}_6\text{H}_{12}''$  decomposes to produce "hot" hydrogen atoms that cannot be scavenged by benzene,



The possibility that  $c\text{-C}_6\text{H}_{12}''$  decomposes to produce molecular hydrogen has not been eliminated, however.

The purpose of the present study was to determine the effect of cyclohexene on the cyclohexane radiolytic system.

#### EXPERIMENTAL

##### Materials

Eastman spectro-grade cyclohexane was used.

Cyclohexene was obtained from Matheson, Coleman, and Bell and from Eastman. The results obtained with the cyclohexene from the two sources were the same within experimental error.

Cyclohexylcyclohexene was prepared by dehydrating 2-cyclohexylcyclohexanol with phosphorus pentoxide and distilling the olefin from the reaction mixture.

<sup>1</sup>Manuscript received January 25, 1960.

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta.

### *Preparation of the Samples*

One- and two-milliliter samples were irradiated in sealed pyrex cells of approximately 2- and 4-ml capacity, respectively.

The cells were filled by conventional vacuum techniques. Briefly, the liquids were measured by pipette and were thoroughly degassed before being distilled into the irradiation cells.

### *Irradiation of the Samples*

The samples were irradiated with  $\text{Co}^{60}$   $\gamma$ -rays. Dose rates were determined with the Fricke dosimeter, using  $G(\text{Fe}^{+++}) = 15.6$  and  $\epsilon(\text{Fe}^{+++} \text{ in } 0.8 \text{ N H}_2\text{SO}_4, 25^\circ \text{C}, 304 \text{ m}\mu) = 2225$ . The dose rates varied from  $5.9 \times 10^{17}$  to  $10.4 \times 10^{17}$  ev/ml hr for the Fricke dosimeter at  $25^\circ \text{C}$ . The amount of energy absorbed per milliliter per hour in the organic liquids was calculated by multiplying the energy absorbed per milliliter per hour in the Fricke dosimeter by the ratio of the electron densities at the appropriate temperatures. The electron densities, at  $24^\circ \text{C}$ , of the Fricke dosimeter, cyclohexane, and cyclohexene were 0.566, 0.442, and  $0.452 \text{ e}^-$  moles/ml, respectively. Temperature corrections were applied when necessary.

### *Analyses*

Gas fractions were separated by distillation at  $-195^\circ \text{C}$  and  $-112^\circ \text{C}$ . Each fraction was collected and measured in a combination Toepler pump - McLeod gauge and then analyzed by gas chromatography. The remaining liquid was also analyzed by gas chromatography.

## RESULTS

The dose received by the samples was  $2.7 \pm 0.5 \times 10^{20}$  ev/ml,  $24^\circ \text{C}$ . Since the slight decrease in most product yields with increasing dose in the pure cyclohexane system is probably due to the accumulation of an inhibitor, the  $G$  values used in this paper for pure cyclohexane will be those obtained by extrapolation to zero dose (1), unless otherwise mentioned.

### *Cyclohexane-Cyclohexene Solutions*

#### *Products Volatile at $-195^\circ \text{C}$*

This fraction consisted of hydrogen and methane. The amounts of methane were too small to measure accurately. For pure cyclohexane  $G(\text{CH}_4) = 0.02$  and the value decreased to less than 0.01 when the electron fraction of cyclohexene,  $\epsilon_e$ , in the solution was greater than about 0.04.

$$[i] \quad \epsilon_e = \frac{46n_e}{46n_e + 48n_c}$$

where  $n_e$  and  $n_c$  are the respective numbers of moles of cyclohexene and of cyclohexane in the solution, and 46 and 48 are the numbers of electrons in a cyclohexene molecule and a cyclohexane molecule respectively.

The hydrogen yield,  $G(\text{H}_2)$ , decreased rapidly as  $\epsilon_e$  was increased from 0 to 0.05 and decreased slowly as  $\epsilon_e$  was increased further (see Fig. 1A).

#### *Products Volatile at $-112^\circ \text{C}$*

This fraction consisted of about 70% ethylene with small amounts of ethane, acetylene, and propylene and traces of propane and butene.

The total yield of the fraction,  $G(-112^\circ\text{C})$ , varied only slightly with  $\epsilon_e$  (see Fig. 1B). For pure cyclohexane, the value of  $G(-112^\circ\text{C})$  decreased very markedly with increasing dose (1), so the value plotted in Fig. 1B is the one that was obtained at a dose of  $2.5 \times 10^{20}$  ev/ml (about the same dose as was received by the solutions). Thus the increase in  $G(-112^\circ\text{C})$  between  $\epsilon_e = 0$  and  $\epsilon_e = 0.026$  may not have much significance.

These results will not be discussed further until they have been investigated more fully.

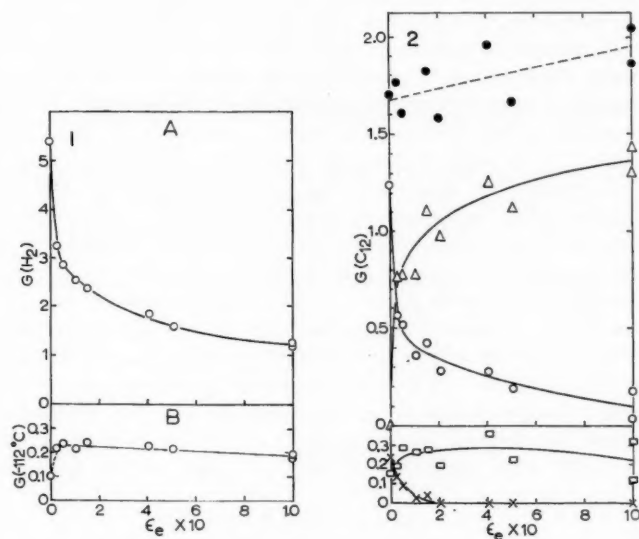


FIG. 1. (A) Variation of hydrogen yield with composition of solution. (B) Variation of yield of  $-112^\circ\text{C}$  gas fraction with composition of solution.  $\epsilon_e$  = electron fraction of cyclohexene in the solution.

FIG. 2. Variation of  $\text{C}_{12}$  hydrocarbon yields with electron fraction of cyclohexene,  $\epsilon_e$ , of solution.  $\circ$  dicyclohexyl;  $\Delta$  dicyclohexenyl;  $\bullet$  total  $\text{C}_{12}$ , measured on Apiezon L column;  $\square$  cyclohexylcyclohexene;  $\times$  cyclohexylhexene.

### Liquid Products

The measured liquid products were dicyclohexyl, cyclohexylcyclohexene, dicyclohexenyl, cyclohexylhexene, and total  $\text{C}_{12}$  hydrocarbons (see Fig. 2). There were no detectable products with carbon numbers between  $\text{C}_6$  and  $\text{C}_{12}$ . Cyclohexane was a product in the pure cyclohexene system and cyclohexene was produced from pure cyclohexane, but these substances could obviously not be measured as products in the irradiated solutions. The maximum amount of decomposition that occurred in any irradiated sample corresponded to about 0.2% of the initial cyclohexane plus cyclohexene.

The dicyclohexyl yield decreased rapidly with increasing cyclohexene concentration at low concentrations ( $0 < \epsilon_e < 0.05$ ) and decreased slowly as the cyclohexene concentration was increased further.

The dicyclohexenyl yield increased rapidly with increasing cyclohexene concentration at low concentrations ( $0 < \epsilon_e < 0.05$ ) and increased slowly as the concentration was increased further.

The cyclohexylcyclohexene yield varied only to a small extent in the region  $0 < \epsilon_e < 1$ .

The cyclohexylhexene yield decreased from 0.23 to zero in the region  $0 \leq \epsilon_e \leq 0.2$ .

The total yield of  $C_{12}$  hydrocarbons, measured on the Apiezon L chromatographic column, increased slightly as  $\epsilon_e$  was increased from 0 to 1. The Apiezon L column did not resolve the dicyclic  $C_{12}$  hydrocarbons but did separate them from isomers containing an open chain.

The total polymer yield was determined for a solution with  $\epsilon_e = 0.405$  by evaporating 1 ml of irradiated solution and 1 ml of unirradiated solution under identical conditions. The weight of each sample was determined as a function of time and the weight vs. time curves were compared. A weight vs. time curve was determined for dicyclohexyl under the same conditions. It was found that  $G(C_6 \text{ units} \rightarrow \text{polymer}) = 4.5$ . This compares with the value 3.9 obtained by gas-chromatographic analysis ( $2 \times G(\text{total } C_{12})$ ). A similar determination of total polymer in irradiated cyclohexene gave  $G(\text{cyclohexene} \rightarrow \text{polymer}) \approx 8$ . Only about four of these units were accounted for by the  $C_{12}$  hydrocarbon analysis. The remaining four units of "other polymer" were probably of higher molecular weight. Manion and Burton (2) determined the polymer yield in irradiated cyclohexene by evaporation and weighing and reported that  $G(\text{cyclohexene} \rightarrow \text{polymer}) = 12.4$ , but that it was difficult to decide when solvent evaporation was complete. It would seem, from the present experiments, that this difficulty was caused by small amounts of intermediate compounds that were present in the original cyclohexene.

The present results are in general agreement with those of Dewhurst (3), who found that, in the presence of  $5.2 \times 10^{-4}$  mole cyclohexene/g solution ( $\epsilon_e = 0.040$ ),  $G(H_2) = 2.9$ ,  $\Delta G(H_2) = -2.4$ ,  $G(c-C_8H_{10}) = -2.3$ , and that the dicyclohexyl yield was unchanged. However, the present results confirm the previous suspicion (1) that Dewhurst's "dicyclohexyl" was not pure dicyclohexyl but probably was a measure of the total  $C_{12}$  hydrocarbons. At  $\epsilon_e = 0.040$  only one third of the  $C_{12}$  hydrocarbons is dicyclohexyl (see Fig. 2).

#### Pure Cyclohexene

The detected products and their yields were as follows:

Product	G	Product	G
Hydrogen	1.2	Dicyclohexenyl	1.36
Ethylene	0.16	Cyclohexylcyclohexene	0.22
Acetylene	0.022	Dicyclohexyl	0.11
$C_4$ hydrocarbon	0.10	Total $C_{12}$ hydrocarbons	1.96
Cyclohexane	1.0	Total polymer	8 cyclohexene units

The cyclohexene from Matheson, Coleman, and Bell contained 0.6 mole % cyclohexane and that from Eastman contained 0.04 mole % cyclohexane. Corresponding corrections were applied before calculating  $G(\text{cyclohexane})$ .

The total  $C_{12}$  hydrocarbons were measured on the Apiezon L column. The total polymer was determined by weighing.

#### DISCUSSION

##### Pure Cyclohexene

If the radiolysis of cyclohexene is considered as



then the total hydrogen deficiency in the yields of the products X should be equal to  $G(H_2) = 1.2$ . It is evident from Table I that the hydrogen equivalent of about one

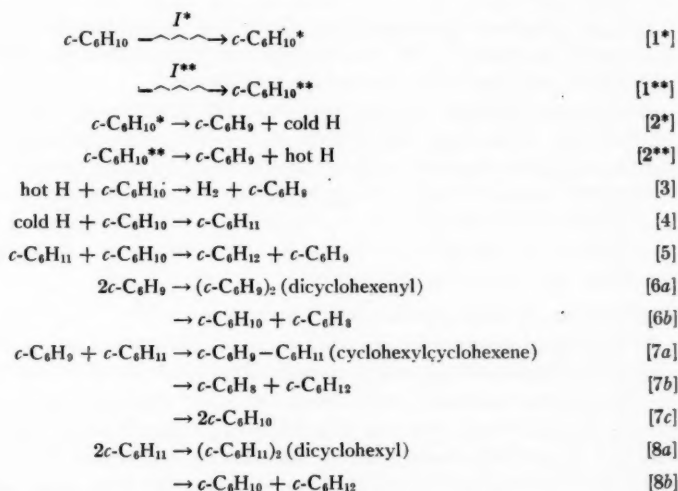
TABLE I  
Material balance of products from irradiation of cyclohexene

Product	G	H <sub>2</sub> equivalent
C <sub>2</sub> + C <sub>4</sub> hydrocarbons	0.28	0.0
Cyclohexane	1.0	-1.0
Dicyclohexenyl	1.36	1.36
Cyclohexylcyclohexene	0.22	0.0
Dicyclohexyl	0.11	-0.11
Other polymer	4.6 C <sub>6</sub> units	?
Total		0.25+?
H <sub>2</sub>	1.2	1.2

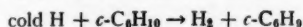
NOTE: The hydrogen equivalent of a product corresponds to the amount of hydrogen that was produced when that product was formed from cyclohexene.

*G* unit of hydrogen-deficient hydrocarbon products have remained unidentified. These products might not be entirely included in the "other polymer" because some possible products, such as cyclohexadiene, might have been missed under the present analytical conditions.

The formation of the major identified products can be explained by the following mechanism.



By analogy with the cyclohexane system (1) it is postulated that there are at least two distinct activated species of cyclohexene. One activated species,  $c\text{-C}_6\text{H}_{10}^*$ , decomposes to produce "cold" hydrogen atoms (reaction [2\*]), while the other activated species,  $c\text{-C}_6\text{H}_{10}^{**}$ , decomposes to produce "hot" hydrogen atoms (reaction [2\*\*]). It is further postulated that the hot hydrogen atoms abstract from cyclohexene according to reaction [3] and that most of the cold hydrogen atoms add to cyclohexene according to reaction [4]. The possibility that  $c\text{-C}_6\text{H}_{12}$  generates molecular hydrogen directly cannot be eliminated by the present experiments, and future work may require the inclusion of such a reaction, perhaps in place of reactions [2\*\*] and [3]. The reaction



may be neglected by comparison with reaction [4]. This will be discussed further in the next section.

The large yield of cyclohexane,  $G(c\text{-C}_6\text{H}_{12}) = 1.0$ , seems to indicate that reaction [5] occurs. Reaction [5] will be mentioned again in the next section.

Although reactions [6b], [7b], [7c], and [8b] probably occur to an appreciable extent their products were not observed. Cyclohexadiene could not be detected by the present analytical technique, cyclohexane appeared to be produced more copiously by reaction [5], and cyclohexene was the starting material.

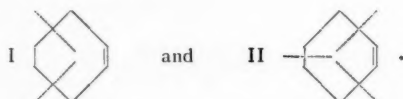
The products of ring fission can be accounted for by the following reactions, if the  $\text{C}_4$  hydrocarbon product is butadiene:



and



Thus  $G(\text{C}_4) + 2G(\text{C}_2\text{H}_2) = 0.144$  agrees fairly well with  $G(\text{C}_2\text{H}_4) = 0.16$ . This involves two types of ring fission



In the liquid phase radiolysis by  $\gamma$ -rays, type I appears to occur four to five times as frequently as type II. Of the cyclohexene molecules that reacted under the present conditions, less than 3% reacted by ring fission.

The "other polymer" might have been produced by ion-molecule reactions. Thus far there seems to be no evidence that ion-molecule reactions are important in the radiolysis of liquid saturated hydrocarbons, but there is evidence that they are important in the radiolysis of liquid olefins, especially in polymer formation (4-6). The possibility that some or all of the identified products were formed by ion-molecule reactions cannot be ruled out by the present results, but their formation can be explained by free radical reactions (see preceding mechanism).

#### Cyclohexane-Cyclohexene Solutions

It has been assumed that, if there were no interaction between the different components of the solution, the cyclohexane product yields would be directly proportional to the electron fraction of cyclohexane,  $\epsilon_e$ , in the solution, and that the cyclohexene product yields would be proportional to  $\epsilon_e$ . This is probably not strictly correct but electron fraction has been used for lack of a better function.

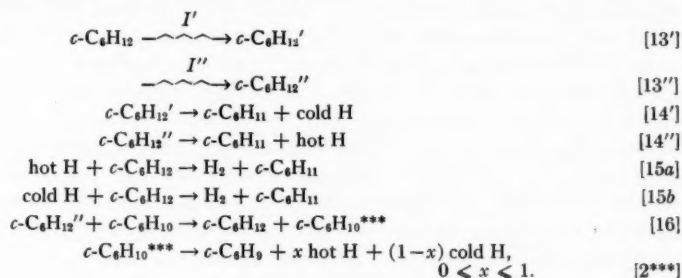
In the cyclohexane-benzene solutions, when the electron fraction of benzene,  $\epsilon_b$ , was increased from zero to 0.027,  $G(\text{H}_2)$  decreased from 5.37 to 3.16 (1). At least 20%, and perhaps all of this decrease, appeared to be due to the scavenging of "cold" hydrogen atoms by benzene. In the cyclohexane-cyclohexene solutions, at  $\epsilon_e = 0.026$ ,  $G(\text{H}_2) = 3.22$ . Thus, at this low concentration of solute, the same amount of decrease is produced in the hydrogen yield from cyclohexane by both benzene and cyclohexene. It is unlikely that the ratio of rate constants,  $k_{11}/k_{12}$ , has the same value when the unsaturate, RH,



is benzene as when it is cyclohexene. It may therefore be concluded that reaction [12] occurs to a negligible extent with the cold hydrogen atoms generated by  $c\text{-C}_6\text{H}_{12}'$ . Reaction [12] can, however, occur with the hot hydrogen atoms generated by  $c\text{-C}_6\text{H}_{12}''$ .



The experimental results were tested against several different mechanisms. The mechanism that appeared to best fit the results included all the reactions [1] to [8] in the pure cyclohexene mechanism plus the reactions



This is essentially the same mechanism as that postulated for the cyclohexane-benzene system (1) except that cyclohexene itself undergoes several reactions that benzene does not (e.g., the benzene counterparts of reactions [2\*], [2\*\*\*], [5], [6a, 6b], and [7a, 7b, 7c] were not observed). In reaction [2\*\*\*] the  $x$  represents the fraction of the  $c\text{-C}_6\text{H}_{10}^{***}$  that decomposes to form hot hydrogen atoms, and hence molecular hydrogen. The value of  $x$  was determined by kinetic analysis (see later). Reaction [15b] could occur in the pure cyclohexane system because the only competing reactions involving the cold hydrogen atoms would be radical combination, and the radical concentrations are very small. The counterpart of reaction [15b] probably occurs to a certain extent in the cyclohexene system, but, as mentioned earlier, it appears to be negligible (within the accuracy of the present experiments) by comparison with reaction [4].

Since the over-all mechanism is complex, the kinetic analysis will be simplified by treating one product at a time. It will be assumed that  $I'$  and  $I''$  are each directly proportional to the electron fraction of cyclohexane,  $\epsilon_e$ , and that  $I^*$  and  $I^{**}$  are each directly proportional to  $\epsilon_e$ .

#### Hydrogen

By analogy with the cyclohexane-benzene system (1), the rapid decrease in hydrogen yield at low cyclohexene concentrations ( $\epsilon_e < 0.05$ ) is largely due to scavenging of the cold hydrogen atoms generated by  $c\text{-C}_6\text{H}_{12}'$ . The slower decrease at higher cyclohexene concentrations is mainly due to energy transfer "protection" of the species  $c\text{-C}_6\text{H}_{12}''$ . These effects may be separated and measured by kinetic analysis. It was found in the cyclohexane-benzene system that  $I'' = (3.0 \pm 0.4)\epsilon_e$  and  $I' = (2.4 \pm 0.4)\epsilon_e$ .

The production of hydrogen involves reactions [1\*\*], [2\*\*], [2\*\*\*], [3], [4], [13'], [13''], [14'], [14''], [15a], [15b], and [16]. Reactions [13'] and [14'] are important mainly at low cyclohexene concentrations. Reactions [1\*] and [2\*] do not contribute appreciably to hydrogen production because, when the cyclohexene concentration is high enough that these reactions occur to an appreciable extent, reaction [4] occurs with great efficiency.

The only reactions involved to an appreciable extent in the production of molecular hydrogen from cold hydrogen atoms are reactions [13'], [14'], [15b], and [4]. The hydrogen yield from this source will be represented as  $G(\text{H}_2)'$  because it is generated by  $c\text{-C}_6\text{H}_{12}'$ . This hydrogen can be scavenged by cyclohexene. Steady-state treatment of the above reactions gives

$$[ii] \quad G(\text{H}_2)' = \frac{I'}{1 + k_4(c\text{-C}_6\text{H}_{10})/k_{15b}(c\text{-C}_6\text{H}_{12})}.$$

For pure cyclohexane the yield of hydrogen is given approximately by the equation

$$[\text{iii}] \quad G(\text{H}_2) = 5.37 - 0.08 \times \text{dose} (10^{20} \text{ ev/ml cyclohexane, } 24^\circ \text{ C})$$

over the dose range 0 to  $2.5 \times 10^{20}$  ev/ml (1). Assuming that this decrease in hydrogen yield with increasing dose is due to the accumulation of cyclohexene in the system, the value of the ratio  $k_4/k_{15b}$  can be determined from equations [ii] and [iii], using  $I' = 2.4\epsilon_e$  and the average value of  $(c\text{-C}_6\text{H}_{10})/(c\text{-C}_6\text{H}_{12})$  over the dose range considered. Over the range 0 to  $2.5 \times 10^{20}$  ev/ml,  $\Delta G(\text{H}_2) = 0.20$  and the average  $(c\text{-C}_6\text{H}_{10})/(c\text{-C}_6\text{H}_{12}) = 4.6 \times 10^{-4}$ . Therefore  $k_4/k_{15b} = 200$ . Guentner, Hardwick, and Nejak (7) concluded, from a comparison of their pure cyclohexane results with the cyclohexane-cyclohexene solution results of Manion and Burton (2), that the accumulated cyclohexene alone was not sufficient to explain the observed decrease in hydrogen yield with increasing dose. Their conclusion may be incorrect, however, because at the concentrations of cyclohexene used by Manion and Burton both energy transfer protection and hydrogen atom scavenging were probably occurring.

Thus the amount of unscavenged hydrogen,  $G(\text{H}_2)'$ , can be calculated from equation [ii] for the various cyclohexene solutions studied, and can be subtracted from the observed hydrogen yield,  $G(\text{H}_2)_{\text{obs}}$ .

In pure cyclohexene  $G(\text{H}_2) = 1.2$  and the only reactions that enter into the production of hydrogen in this system are reactions [1\*\*], [2\*\*], and [3]. It may therefore be assumed that the amount of hydrogen resulting from the direct excitation of cyclohexene,  $G(\text{H}_2)^{**}$ , is given by

$$[\text{iv}] \quad G(\text{H}_2)^{**} = I^{**} = 1.2\epsilon_e.$$

The amount of hydrogen that results from the initial formation of  $c\text{-C}_6\text{H}_{12}''$ ,  $G(\text{H}_2)''$ , can then be determined from

$$[\text{v}] \quad G(\text{H}_2)'' = G(\text{H}_2)_{\text{obs}} - G(\text{H}_2)' - G(\text{H}_2)^{**}.$$

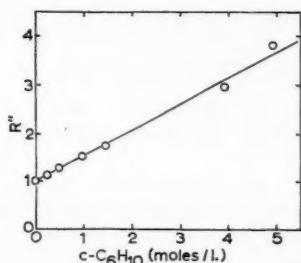
This hydrogen cannot be scavenged by cyclohexene but  $G(\text{H}_2)''$  may be decreased by energy transfer from  $c\text{-C}_6\text{H}_{12}''$  to cyclohexene, provided that all the excited cyclohexene molecules,  $c\text{-C}_6\text{H}_{10}^{***}$ , so formed do not decompose to produce hot hydrogen atoms and hence molecular hydrogen. Only reactions [13''], [14''], [15a], [16], [2\*\*\*], and [3] enter into the production of hydrogen from this source. Steady-state treatment of these reactions gives

$$[\text{vi}] \quad G(\text{H}_2)'' = I'' \left[ \frac{k_{14}'' + x k_{16}(c\text{-C}_6\text{H}_{10})}{k_{14}'' + k_{16}(c\text{-C}_6\text{H}_{10})} \right],$$

which may be rearranged to

$$[\text{vii}] \quad [1 + y(c\text{-C}_6\text{H}_{10})] I'' / G(\text{H}_2)'' = 1 + k_{16}(c\text{-C}_6\text{H}_{10}) / k_{14}'', \\ = R'',$$

where  $y = x k_{16}/k_{14}''$ ,  $x$  = fraction of  $c\text{-C}_6\text{H}_{10}^{***}$  that decomposes to form hot hydrogen atoms and hence molecular hydrogen, and  $R''$  represents the left-hand side of equation [vii]. Various sets of  $R''$  were calculated, using  $I'' = 3.0\epsilon_e$  and various values of  $y$ , and each set of  $R''$  values was plotted against cyclohexene concentration (moles/l.). The best straight line was obtained with  $y = 0.3$  (see Fig. 3). The slope of the line gives  $k_{16}/k_{14}'' = 0.54 \text{ l./mole}$ . Therefore  $x = 0.56$ .

FIG. 3. Variation of  $R''$  with cyclohexene concentration.

$$R'' = [1 + y(c\text{-C}_6\text{H}_{10})]I''/G(\text{H}_2)'',$$

Since the cyclohexane-benzene system would allow  $I''$  to have a value in the range  $(3.0 \pm 0.4)\epsilon_e$ , the best value being  $3.0\epsilon_e$ , the above kinetic analysis was repeated for the cyclohexane-cyclohexene system using various sets of values of  $I''$  and  $I' = (5.4 - I'')\epsilon_e$ . The corresponding value of  $k_4/k_{16b}$  was calculated for each set and the numerical and graphical analysis was done as described above. It was found that the present system would allow  $I'' = (3.0 \pm 0.3)\epsilon_e$ . Therefore  $I' = (2.4 \mp 0.3)\epsilon_e$ ,  $k_4/k_{16b} = 200 \pm 30$ , and  $x = 0.56 \pm 0.10$ , but  $k_{16}/k_{14}'' = 0.54 \pm 0.4$  l./mole. The experimental value of  $k_{16}/k_{14}''$  is much more flexible than are the other experimentally determined constants. The ratio  $k_{16}/k_{14}''$  in the present system corresponds to the previously reported  $k_3''/k_4''$  in the cyclohexane-benzene system (1). Similar analysis of the latter system gave  $k_3''/k_4'' = 0.78 \pm 0.11$  l./mole, which is relatively clearly defined. The main reason for the difference in precision of determination of the value of this ratio of rate constants in the two systems seems to be the presence of the extra adjustable parameter,  $x$ , in the cyclohexene system, together with a slightly lower precision in the measured hydrogen yields in this system.

*Dicyclohexyl, Cyclohexylcyclohexene, and Dicyclohexenyl*

Since cyclohexyl radicals are produced when the cold hydrogen atoms are scavenged by cyclohexene, the observed sharp decrease in dicyclohexyl yield in the region  $\epsilon_e = 0$  to  $0.026$  was probably caused by the reaction of cyclohexyl radicals with cyclohexene (reaction [5]). This would also explain the sharp increase in dicyclohexenyl yield in this region.

The rates of formation of these three products are given by

$$[\text{viii}] \quad d(\text{dicyclohexyl})/dt = k_{8a}(c\text{-C}_6\text{H}_{11})^2,$$

$$[\text{ix}] \quad d(\text{cyclohexylcyclohexene})/dt = k_{7a}(c\text{-C}_6\text{H}_{11})(c\text{-C}_6\text{H}_9),$$

and

$$[\text{x}] \quad d(\text{dicyclohexenyl})/dt = k_{6a}(c\text{-C}_6\text{H}_9)^2.$$

Since the rates of formation of the products are related to their  $G$  values by the same proportionality constant,

$$[\text{xi}] \quad \frac{k_{7a}}{(k_{8a}k_{6a})^{1/2}} = \frac{G(\text{cyclohexylcyclohexene})}{[G(\text{dicyclohexyl}) G(\text{dicyclohexenyl})]^{1/2}}.$$

The values of this ratio, calculated from equation [xi], at the various cyclohexene concentrations, are

$\epsilon_0$	0.026	0.051	0.102	0.153	0.204	0.405	0.506	1.00
$k_{71a}/(k_{8a}k_{9a})^{\frac{1}{2}}$	0.30	0.44	0.49	0.40	0.37	0.59	0.48	0.56

The average value is  $0.45 \pm 0.08$ .

#### *Cyclohexylhexene*

The cyclohexylhexene yield varied with cyclohexene concentration (Fig. 2) in the same way it did with benzene concentration (reference 1). The previously postulated reactions which affect the yield of this product appear to apply equally well when cyclohexene is substituted for benzene.

#### *Total C<sub>12</sub> Hydrocarbons*

The variation of the total C<sub>12</sub> hydrocarbon yield with cyclohexene concentration is the main evidence that the protection of cyclohexane by cyclohexene is sacrificial, i.e. that a cyclohexene molecule decomposes for each cyclohexane molecule that is "protected".

#### ACKNOWLEDGMENTS

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## RELATIVE RATES OF REACTION OF OZONE WITH OLEFINS IN THE VAPOR PHASE<sup>1</sup>

T. VRBASKI<sup>2</sup> AND R. J. CVETANOVIĆ

### ABSTRACT

Relative rates of reaction of ozone with a number of olefins in the vapor phase have been determined by the use of the competitive method and GLC analysis of the reaction products. The results indicate a basic electrophilic trend onto which is superimposed a trend due to a partially inhibiting effect of the substituent groups, in particular of those on the more substituted carbon atom of the olefinic double bond. The results are discussed particularly in terms of a two-step addition process, involving an initial formation of an ozone-olefin  $\pi$ -complex and a slower rearrangement of the  $\pi$ -complex into the cyclic "initial ozonide".

### INTRODUCTION

A study of the relative rates of reactions of oxygen atoms with olefins in the vapor phase has been recently carried out in this laboratory (1), and some aspects of these reactions are still under investigation. This study uncovered simple correlations of the logarithms of the rate constants with some physical properties of the olefins and established experimentally the electrophilic character of oxygen atoms in their reactions with olefins. The results of this vapor phase investigation were compared with some other series of electrophilic reactions in solution and with the very few literature values available at the time for the vapor phase reactions of ozone with olefins. On this basis, nothing could be said with certainty about the reagent character which ozone exhibited in its reactions with olefins, although qualitatively an electrophilic trend was known from the work of Wibaut and his co-workers (2) for ozone in reactions with some aromatic compounds.

In view of the potentially useful information which comparative studies of this kind may provide, it was thought of interest to attempt to obtain the relative rates of ozone reactions with a number of representative olefins. In the course of this investigation, some information was obtained on the products formed in these reactions under the particular experimental conditions employed, and, this part of the work has already been described (3) (referred to in the following as Part I). In the present communication the relative rate constants obtained for these reactions are reported and their trends with olefin structure discussed.

### EXPERIMENTAL

The reaction system, the method of analysis, and apart from some additional detail, the general experimental procedures used in this work have been already described in Part I. In present case pairs of olefins in various concentration ratios were introduced into the 188-cc spherical reaction vessel. Their total amount was in most experiments 400  $\mu$ moles to which was subsequently added the equivalent of 25  $\mu$ moles of ozone. This was done by admitting slowly the required pressure of ozonized oxygen (2.6 to 3.2% by volume of ozone) into the mixture of olefin vapors at  $25 \pm 2^\circ$ . The total pressure was therefore 110 to 135 mm. In some experiments, especially in the case of *cis*-2-butene, *trans*-2-butene, and tetramethyl ethylene, the total amount of the two olefins was reduced

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to 200  $\mu$ moles, to which then only the equivalent of 10  $\mu$ moles of ozone was added and the total pressure was 50 to 60 mm. These smaller amounts were used in order to decrease the excess quantities of the original olefins remaining at the end of the reaction and thus to make easier the subsequent analysis of the products by gas-liquid chromatography (GLC).

The olefins used were of the highest available grade and were freed of any peroxides present and thoroughly degassed and bulb-to-bulb distilled *in vacuo*. A mercury gauge was used to measure the pressures; this was separated from the rest of the reaction system by two ice traps in order to minimize the concentration of mercury vapor. As described in Part I, no noticeable decrease in ozone concentration resulted from the small amount of mercury vapor present. Silicone grease was used for the stopcocks in the parts of the system exposed to ozone-oxygen mixtures.

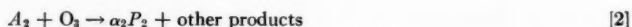
The products were frozen out in two liquid nitrogen traps in series while excess oxygen and any noncondensable products were pumped off slowly through a capillary constriction. The condensable products were then transferred to GLC. In some instances excess olefins were removed beforehand on a Le Roy still (4). The details of the GLC arrangements used have been given in Part I.

### RESULTS

The method of competing reactions has been used to determine the relative rates of the reactions of ozone with various olefins. This has been done by comparing the GLC peak areas of the major carbonyl compounds formed from two olefins ( $\Delta P_1$  and  $\Delta P_2$ , respectively) at different ratios of their initial concentrations ( $[A_2]_1/[A_1]_1$ ). If the two competing reactions are



and



and if the initial concentrations of the two olefins are sufficiently high so that they remain essentially unaltered in the course of the reaction, then the ratio of the rate constants may be derived from the expression

$$[3] \quad \frac{\Delta P_1}{\Delta P_2} = \frac{k_1 \alpha_1 [A_1]_1}{k_2 \alpha_2 [A_2]_1}$$

A plot of  $\Delta P_1/\Delta P_2$  vs.  $[A_1]_1/[A_2]_1$  should be linear with zero intercept and the slope is then  $(k_1/k_2) (\alpha_1/\alpha_2)$ . To get the ratio of the rate constants, the ratio  $\alpha_1/\alpha_2$  has to be known. This is determined from the amounts of products formed ( $\Delta P^*$ ) when each of the two olefins is taken singly, i.e.  $\alpha = \Delta P^*/\Delta O_3$  and  $\alpha_1/\alpha_2 = \Delta P_1^*/\Delta P_2^*$  provided the same amount of ozone is used in the two "single" runs and ozone is consumed exclusively in reactions [1] and [2]. This last requirement is presumably met when relatively large concentrations of olefins are used.

Under similar conditions also  $\Delta P_1/\alpha_1 + \Delta P_2/\alpha_2 = \Delta P_1^*/\alpha_1$ , so that

$$[4] \quad \frac{\Delta P_1}{\Delta P_1^* - \Delta P_1} = \frac{k_1 [A_1]_1}{k_2 [A_2]_1}$$

an alternative expression which can be used when  $\Delta P_2$  cannot be measured.

In most of the present work use was made of eq. [3]. Fairly good linear plots through the origin were obtained as shown in Figs. 1, 2, and 3, and the slopes divided by the corresponding  $\alpha_1/\alpha_2$  values gave the relative rate constants  $k_1/k_2$  summarized in Table I.



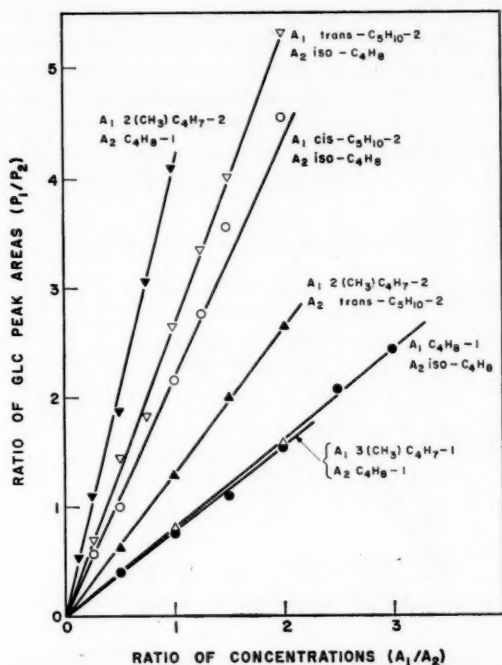


FIG. 1. Determination of the ratios of rate constants for 2-methyl-2-butene and 1-butene, *trans*-2-pentene and isobutene, *cis*-2-pentene and isobutene, 2-methyl-2-butene and *trans*-2-pentene, 1-butene and isobutene, 3-methyl-1-butene and 1-butene.

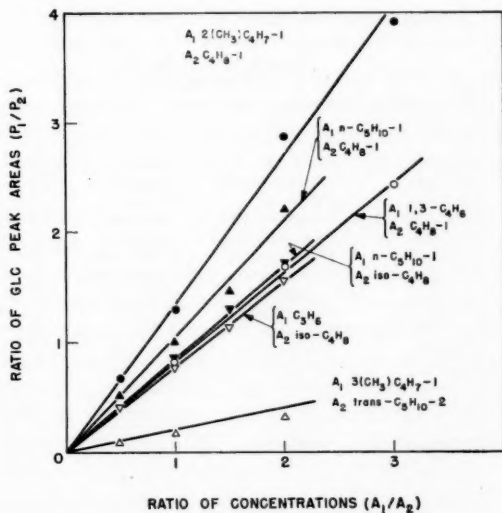


FIG. 2. Determination of the ratios of rate constants for 2-methyl-1-butene and 1-butene, *n*-1-pentene and 1-butene, *n*-1-pentene and isobutene, 1,3-butadiene and 1-butene, propylene and isobutene, 3-methyl-1-butene and *trans*-2-pentene.

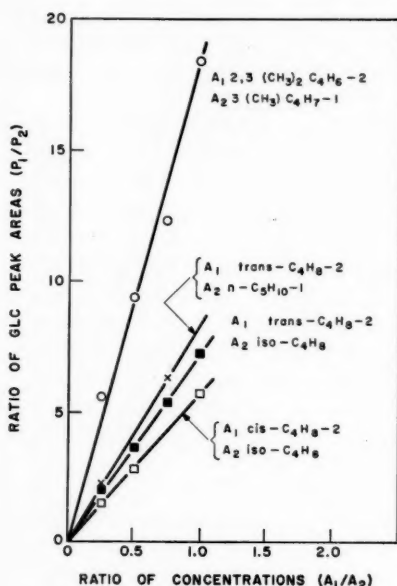


FIG. 3. Determination of the ratios of the rate constants for 2,3-dimethyl-2-butene and 3-methyl-1-butene, *trans*-2-butene and *n*-1-pentene, *trans*-2-butene and isobutene, *cis*-2-butene and isobutene.

TABLE I

The mean values of the ratios of the rate constants

	Reactant olefins		Products used for rate determinations		$\alpha_1/\alpha_2$	Mean, $k_1/k_2$	Equation used
	$A_1$	$A_2$	$P_1$	$P_2$			
1	$C_2H_4$	iso- $C_4H_8$	—	Acetone	—	0.51	4, 4a
2	$C_2H_4$	iso- $C_4H_8$	Acetaldehyde	Acetone	0.551	1.41	3
3	$C_4H_8-1$	iso- $C_4H_8$	Propanal	Acetone	0.749	1.07	3
4	<i>cis</i> - $C_4H_8-2$	iso- $C_4H_8$	Acetaldehyde	Acetone	1.53	3.69	3, 3a
5	<i>trans</i> - $C_4H_8-2$	iso- $C_4H_8$	Acetaldehyde	Acetone	1.58	4.56	3, 3a
6*	<i>trans</i> - $C_4H_8-2$	<i>n</i> - $C_5H_{10}-1$	Acetaldehyde	<i>n</i> -Butanal	1.94	4.24	3, 3a
7	1,3- $C_4H_6$	<i>n</i> - $C_4H_8-1$	Acroleine	Propanal	0.726	1.07	3
8	<i>n</i> - $C_5H_{10}-1$	<i>n</i> - $C_4H_8-1$	<i>n</i> -Butanal	Propanal	1.05	1.00	3
9*	<i>n</i> - $C_5H_{10}-1$	iso- $C_4H_8$	<i>n</i> -Butanal	Acetone	0.789	1.06	3
10	<i>cis</i> - $C_5H_{10}-2$	iso- $C_4H_8$	Propanal	Acetone	0.763	2.84	3, 3a
11	<i>trans</i> - $C_5H_{10}-2$	iso- $C_4H_8$	Propanal	Acetone	0.756	3.50	3, 3a
12	2-( $CH_3$ ) $C_4H_7-1$	<i>n</i> - $C_4H_8-1$	$CH_3 \cdot CO \cdot C_2H_5$	Propanal	1.28	1.03	3
13*	3-( $CH_3$ ) $C_4H_7-1$	<i>n</i> - $C_4H_8-1$	Isobutanol	Propanal	0.985	0.79	3
14	3-( $CH_3$ ) $C_4H_7-1$	<i>trans</i> - $C_5H_{10}-2$	Isobutanol	Propanal	0.928	0.22	3
15*	2-( $CH_3$ ) $C_4H_7-2$	<i>n</i> - $C_4H_8-1$	Acetone	Propanal	1.35	3.02	3, 3a
16	2-( $CH_3$ ) $C_4H_7-2$	<i>trans</i> - $C_5H_{10}-2$	Acetone	Propanal	1.31	0.99	3
17	2,3-( $CH_3$ ) $C_4H_8-2$	3-( $CH_3$ ) $C_4H_7-1$	Acetone	Isobutanol	4.06	4.50	3, 3a
18	<i>n</i> - $C_6H_{12}-1$	iso- $C_4H_8$	—	Acetone	—	1.28	4
19	Cyclohexene	iso- $C_4H_8$	—	Acetone	—	3.74	4, 4a

\*Asterisks indicate the experiments for the cross-checking of the values of  $k_1/k_2$ .

The reaction products  $P_1$  and  $P_2$  and the values obtained for  $\alpha_1/\alpha_2$  are shown and the equation used indicated.

For the pairs of olefins ethylene and isobutene, *n*-1-hexene and isobutene, and cyclohexene and isobutene, the relative rate constants were determined from measurements of the GLC peak areas of acetone (formed from isobutene) using eq. [4]. Fairly good linear plots through the origin are again obtained, as shown in Fig. 4, and the values of  $k_1/k_2$  evaluated from the slopes are shown in Table I.

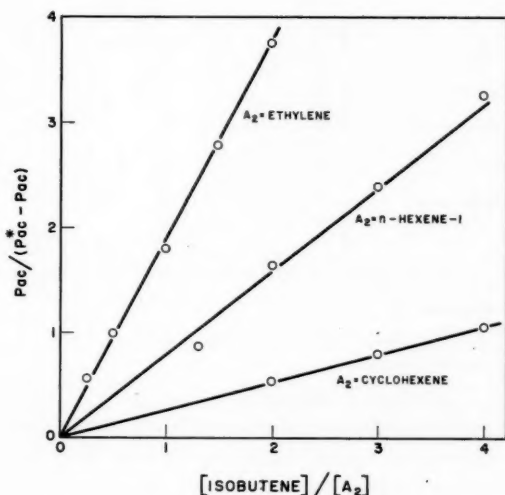


FIG. 4. Determination of the ratios of the rate constants based on eq. [4] for ethylene and isobutene, *n*-1-hexene and isobutene, cyclohexene and isobutene.

In some instances there was appreciable deviation from the assumed constancy of the concentrations of the olefins and the more complex logarithmic expressions (1) instead of eqs. [3] and [4] (referred in Table I as eqs. [3a] and [4a], respectively) were then used to calculate the ratios of the rate constants. However, this led only to relatively small corrections.

There is a satisfactory mutual consistency of the  $k_1/k_2$  values in the cases where cross determinations (marked in Table I with asterisks) have been made. For example, the value for *trans*-2-butene and *n*-1-pentene from run 6 is 4.2 and it is 4.4 when calculated from runs 5, 8, and 3; the value for *n*-1-pentene and isobutene in run 9 is 1.06 and it is 1.07 when calculated from runs 8 and 3; for 3-methyl-1-butene and 1-butene the value is 0.79 in run 13 and 0.70 calculated from runs 14, 11, and 3; for 2-methyl-2-butene and 1-butene it is 3.02 from run 15 and 3.23 calculated from runs 16, 11, and 3.

In Table II are listed the relative rate constants obtained in the present work taking the value for ethylene as unity. The absolute rate constants are then calculated by adopting the value of Cadle and Schadt (5) for ethylene ( $1.8 \times 10^3$  l. mole<sup>-1</sup> sec<sup>-1</sup>) and these are compared with the determinations of Cadle and Schadt (5), of Hanst *et al.* (6), and of Saltzman (7).

TABLE II

The relative rate constants of the ozone-olefin reactions and comparison with the literature values of the absolute rate constants at room temperature

Olefin	Relative rate constants (ethylene = 1)	Absolute rate constants (l. mole <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>-3</sup> )	
		Present work <sup>a</sup>	Literature
Ethylene	1.00	1.8	1.8, <sup>b</sup> 0.8 <sup>c</sup>
Propylene	2.78	5.1	3.8, <sup>b</sup> 4.9 <sup>c</sup>
1-Butene	2.12	3.9	
<i>n</i> -1-Pentene	2.11	3.9	3.2, <sup>b</sup> 4.5 <sup>c</sup>
<i>n</i> -1-Hexene	2.52	4.6	6.1, <sup>b</sup> 6.1, <sup>c</sup> 5.5 <sup>d</sup>
3-Methyl-1-butene	1.65	3.0	
Isobutene	1.97	3.6	3.7 <sup>c</sup>
2-Methyl-1-butene	2.19	4.0	
<i>cis</i> -2-Butene	7.26	13	29 <sup>c</sup>
<i>trans</i> -2-Butene	8.98	17	
<i>cis</i> -2-Pentene	5.59	10	98 <sup>c,e</sup>
<i>trans</i> -2-Pentene	6.90	13	
Cyclohexene	7.37	14	35 <sup>b</sup>
Trimethyl ethylene	6.39	12	
Tetramethyl ethylene	7.49	14	
Butadiene	2.26	4.2	4.9 <sup>c</sup>

<sup>a</sup>Calculated from the relative values in column 1 by adopting for ethylene the value of Cadle and Schadt (1.8 × 10<sup>3</sup> l. mole<sup>-1</sup> sec<sup>-1</sup>, reference 5).

<sup>b</sup>Cadle and Schadt, reference 5.

<sup>c</sup>Hanst *et al.*, reference 6.

<sup>d</sup>Saltzman, reference 7.

<sup>e</sup>Mixture of *cis*- and *trans*-2-pentene.

#### DISCUSSION

The trend in the rate constants of ozone reactions with olefins obtained in the present work agrees for several olefins quite well with the corresponding literature values, as is seen in Table II. At the same time, the literature values for cyclohexene, *cis*-2-butene, and 2-pentene are considerably larger, in particular so the much larger value for 2-pentene. The reasons for these discrepancies are not clear, although some of the potential difficulties inherent in experimental studies of these complex reactions have been briefly discussed in Part I. Further experimental work will be necessary to clarify this point, and in the meantime parts of the following discussion of the relative rate constants obtained in the present work must be regarded as of a tentative character.

The question to which a study of the trends in the rate constants with the olefin structure is hoped to answer is whether in its reactions with alkenes ozone behaves as an electrophilic, nucleophilic, or radical reagent. For aromatic compounds Wibaut and his co-workers (2) have already shown that the qualitative trend is such as expected for an electrophilic reagent. This has been recently further confirmed by a study of the trend in the rates in polyalkyl benzenes, although a concurrent screening effect by the bulkier substituent groups has also been indicated (8).

A qualitative inspection of the relative values in Table II shows that in its reactions with olefins in the vapor phase ozone appears also to behave as an electrophilic reagent. A radical reagent would be expected to react much more rapidly with butadiene, and a nucleophilic reagent would exhibit a trend in the rates opposite to that observed as the number of substituents in the ethylene molecule is increased. However, there are also some irregularities in the trends: for electrophilic reagents the rates of  $\alpha,\alpha$ -disubstituted ethylenes such as isobutene should be approximately equal to those of the  $\alpha,\beta$ -disubstituted derivatives (such as 2-butene) and here they are appreciably smaller. Also the rates of trimethyl and tetramethyl ethylene should be greater than those of the  $\alpha,\beta$ -disubstituted ethylenes while the observed values are about equal.

As reported in a previous publication (1) mutual linear  $\log k - \log k$  (free energy) plots can be constructed for the reactions of some electrophilic reagents with olefins. A similar plot for ozone reactions (Fig. 5) shows appreciable scatter and in particular the points

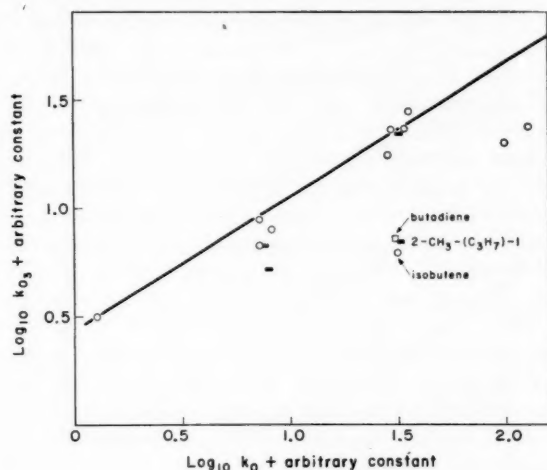


FIG. 5. The "free energy" plot ( $\log k$  vs.  $\log k$ ) for the reactions of ozone and oxygen atoms with olefins.  $k_{O_3}$  are the relative rate constants of the reactions of ozone with olefins and  $k_O$  are the relative rate constants of the corresponding oxygen atom reactions. Filled rectangles represent values for  $k_O$  not known experimentally but estimated approximately from the general trends established for such reactions (reference 1).

for butadiene, isobutene, and 2-methyl-1-butene deviate very strongly. (In this plot some values for  $\log k_O$ , i.e. for the corresponding oxygen atom reactions, are not known and have been approximately estimated—they are indicated in Fig. 5 by filled rectangles.)

Intuitively a correlation may be anticipated between the rates of reactions of electrophilic reagents with olefins and the ionization potentials of the latter. The existence of an approximate linear dependence of the  $\log k$  values for some electrophilic reagents on the ionization potentials of the olefins has been pointed out before (1). This is illustrated again in Fig. 6, which also incorporates some additional experimental values and the data of Doering and Henderson (9) for  $CCl_2$  and  $CBr_2$ , the latter instead of those of Skell and Garner (10) because of the potentially more accurate analytical procedure used in the more recent work. The values for the ozone reactions have also been plotted and there is evidently a large scatter of points, although the general trend appears to be of an electrophilic reagent.

The apparent irregularities and scatter of points for the ozone plot in Fig. 6 can be qualitatively explained by a superposition on a general electrophilic trend of a partly inhibiting effect by the substituent groups. This inhibiting effect could be due to a screening by the substituent groups (steric hindrance) as has been suggested for the reactions of ozone with some aromatics (8) (polyalkyl benzenes). In this case the deviations in Fig. 6 from the values such as indicated for example by the interrupted line may be qualitatively explainable: on the whole the deviations tend to become progressively greater as a screening effect might be expected to become greater. The case of butadiene would be somewhat difficult to explain on that basis, but it is doubtful whether this fact alone could be taken to invalidate a general explanation of this kind.

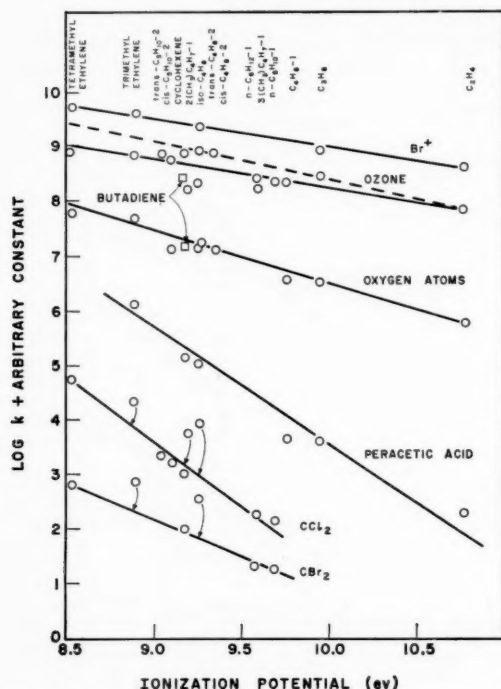
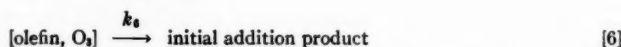


FIG. 6. Plots of  $\log k$  for several series of electrophilic reactions with olefins against the ionization potentials of the olefins.

The sources of data are: ionization potentials: Collin and Lossing, *J. Am. Chem. Soc.* **81**, 2064 (1959), and, for 1-hexene, Honig, *J. Chem. Phys.* **16**, 105 (1948); bromination reactions: Anantakrishnan and Ingold, *J. Chem. Soc.* 984, 1396 (1935); ozone reactions: present work; oxygen atom reactions: Cvetanović, reference 1 and some unpublished data; peracetic acid reactions: Böseken and Stuurman, *Rec. trav. chim.* **56**, 1034 (1937), Böseken and Hanegraff, *Rev. trav. chim.* **61**, 69 (1942), Swern, *J. Am. Chem. Soc.* **69**, 1692 (1947);  $\text{CCl}_2$  and  $\text{CBr}_2$ : Doering and Henderson, reference 9.

A superposition of an additional structural effect on an electrophilic trend could be caused by such a direct screening of the double bond by the substituent groups and the consequent decreased efficiency of a single step attack. Also, it may be due to a more complex addition process, represented for example by the following two-step reaction sequence:



Under such conditions the observed rate constant  $k_{\text{O}_3}$  is a composite quantity

$$[7] \quad k_{\text{O}_3} = k_5 / (1 + k_{-5}/k_6)$$

and when  $k_6$  is small relative to  $k_{-5}$ ,

$$[8] \quad k_{\text{O}_3} = \frac{k_5}{k_{-5}} k_6 = K k_6$$



where  $K$  is the equilibrium constant of reaction [5] and is therefore a measure of stability of the postulated olefin-ozone complex formed in the primary step. This complex would have to be of the nature of a " $\pi$ -complex" since no isomerization of *cis*-2-butene to the *trans* isomer was found under the reaction conditions, as reported in Part I. The electrophilic character of ozone is then readily explained by the dependence of  $k_{O_3}$  on  $K$ , i.e. on the basicity of the olefins.

The retarding effect of the substituents on reaction [6], i.e. on the rearrangement of the  $\pi$ -complex into the initial addition product (the "initial ozonide"), may again be predominantly due to steric inhibition. Alternatively, the inductive effects of the substituents on the more substituted carbon atom of the double bond, the most probable position of the nucleophilic ring closure necessary for the formation of the "initial ozonide", may play a contributing and perhaps a decisive role in determining the rate of reaction [6]. This last possibility has some distinctly attractive features. It can readily explain the exceptionally low values of the rate constants of the reactions of ozone with such compounds as butadiene and isobutene, and, in contrast to this, the fast reactions with  $\alpha,\beta$ -disubstituted olefins.

In view of eq. [8], a trend in  $\log k_{O_3}$  for various olefins is a superposition of the trend in  $\log K$ , which parallels the basicity of the olefins, and of  $\log k_t$ , which incorporates an inhibiting effect. If it is assumed that (a) this inhibiting effect is absent in ethylene, (b) that it is four times\* as large for tetramethyl ethylene, i.e. when the more substituted carbon carries two methyl groups, as for propylene, in which it carries only one methyl group, and (c) that  $\log K$  is a linear function of the ionization potentials of the olefins, it is then possible to calculate the corresponding values of the inhibiting effects for the other olefins. These represent the additive corrections in  $\log_{10}$  units ( $\Delta$ ) which have to be made in order to obtain a linear plot of  $(\log k_{O_3} + \Delta)$  against the ionization potentials. A fair consistency is obtained under such conditions for the olefins which have only methyl radicals as the substituents, with  $\Delta$  of about 0.23 when one methyl radical is present and about four times as much when two methyl radicals are present on the more substituted carbon. On the same basis the values of  $\Delta$  for some other radicals (when present singly on the more substituted carbon) were about 0.55 for  $C_2H_5$ ,  $n-C_3H_7$ , and  $n-C_4H_9$ ; 0.75 for *sec*- $C_3H_7$ ; 0.42 for cyclohexene; and 0.93 for  $C_2H_3$  in butadiene.

While the present results appear to be most logically explainable in terms of the two-step mechanism defined by reactions [5] and [6] and an emphasis is placed on this interpretation, they do not represent a definite proof of validity of such a mechanism. Experimentally, it seems to be difficult to discriminate with certainty between a two-step and a one-step addition mechanism. The conflicting views have been recently reviewed and discussed in some detail by Bailey (11). The two-step mechanism discussed in the present work incorporates the features of the  $\pi$ -complex mechanism outlined by Bailey (12) and, in addition, it specifies the kinetics of the process. However, it does not attempt to differentiate between a five-membered ring structure for the "initial ozonide" and the four-membered ring ("molozone") favored by Bailey (12).

Of the six series of reactions plotted in Fig. 6 only those of oxygen atoms and of ozone are gas phase reactions. The other reactions, all carried out in solution, are in principle subject to complexities resulting from solvent effects. For bromination and peracetic acid reactions there appear to be no pronounced irregularities which could be ascribed to such effects although it would be desirable to have the values of the rate constants for a greater variety of olefins. The reaction series for  $CCl_2$  and  $CBr_2$  additions to olefins

\*The over-all consistency requires this value to be about 4 to 4.5.

appear at first sight to show no correlation with the ionization potentials, as was stressed by Doering and Henderson (9) at the time when the relative rate constants for these two reaction series were reported by these authors. At the same time, there appears to be a significant similarity in the pattern of the plots for these two species in Fig. 6. The meaning of deviations from the lines arbitrarily drawn in Fig. 6 through the experimental points so as to connect most of the points is not clear. The same compounds "deviate" (are too fast relative to the arbitrarily drawn lines) in both series and it is of interest that at least two of these, isobutene and 2-methyl-1-butene, both  $\alpha,\alpha$ -disubstituted ethylenes, strongly deviate in the case of ozone reactions as well (perhaps best shown in Fig. 5) but in the opposite direction, being too slow in comparison with the  $\alpha,\beta$ -disubstituted ethylenes. It is not possible to say at present how far-reaching these analogies and contrasts are until experimental information on the rates of reaction of such reagents with a greater number of olefins becomes available.

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# A STUDY OF THE PRODUCTS OF THE REACTIONS OF OZONE WITH OLEFINS IN THE VAPOR PHASE AS DETERMINED BY GAS-LIQUID CHROMATOGRAPHY<sup>1</sup>

T. VRBASKI<sup>2</sup> AND R. J. CVETANOVIĆ

## ABSTRACT

A broad comparative survey has been made of the products of the vapor phase reactions of ozone with ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 3-methyl-1-butene, isobutene, 2-methyl-1-butene, *cis*-2-butene, *trans*-2-butene, *cis*-2-pentene, *trans*-2-pentene, trimethyl ethylene, tetramethyl ethylene, cyclohexene, and 1,3-butadiene as determined by gas-liquid chromatography and, to a smaller extent, by other analytical methods.

## INTRODUCTION

Ozonization of olefinic compounds in the liquid phase has been the subject of numerous investigations. This extensive field has been adequately reviewed, in particular recently by Bailey (1). The corresponding reactions in the vapor phase are of greater complexity and have received considerably less attention. The recent recognition of their importance in the photochemically induced processes in polluted atmosphere leading to "smog" formation has been largely responsible for the renewed interest in these reactions (2-6).

In connection with current studies of the correlation of the rates of the olefin-oxygen atom reactions with the molecular structure of the olefins (7), it was thought of interest to attempt to obtain the relative rates of the corresponding olefin-ozone reactions. In the course of this study a certain amount of information has been accumulated on the products of a number of olefin-ozone reactions in the vapor phase. A brief report of these results is given in the present paper.

## EXPERIMENTAL

The reactions were carried out at room temperature in a spherical reaction vessel 188 cc in volume, incorporated in a conventional high vacuum apparatus. A batch procedure was employed. The olefin was first transferred into the reaction vessel by freezing in liquid nitrogen and was subsequently vaporized by warming up to room temperature. The required amount of oxygen, containing 2.6 to 3.2% by volume of ozone, was then allowed to stream slowly into the reaction vessel. It was found that at least in some cases, especially when ozone concentration exceeded 3.2%, too rapid introduction of ozone-oxygen mixture could initiate virtually complete combustion of the reacted olefin to carbon dioxide and water accompanied by substantial warming of the reaction vessel and occasional light emission.

Ozone was freshly produced for each run in a standard Towers ozone apparatus by silent electric discharge at 7500 volts and 15 milliamperes. Cylinder oxygen dried over phosphorous pentoxide was used. The ozone concentration was determined iodometrically in the stream of oxygen as it leaves the ozonizer and also immediately prior to the reaction vessel. The two values agreed within the experimental error. The olefins used were of the highest available grade and were thoroughly degassed and bulb-to-bulb distilled *in vacuo* before use.

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<sup>2</sup>National Research Council Postdoctorate Fellow, 1957-59.

The initial amounts of olefins and ozone were 400 and 100  $\mu$ moles and in some cases these quantities were reduced to facilitate the analysis of the products to 200 and 25  $\mu$ moles, respectively. The total pressure in the reaction vessel was, therefore, 360 to 440 mm in the former and 100 to 130 mm in the latter case. A mercury gauge was used to measure the pressures of the reactants, but attempt was made to bring ozone in contact with mercury as little as possible and the slight consumption of ozone in the reaction with some mercury vapor present did not decrease its concentration noticeably.

The condensable reaction products were retained by pumping off the non-condensable gas slowly, using a capillary constriction, through two liquid nitrogen traps in series. No attempt was made to analyze the non-condensable gas which contained the huge excess of oxygen. The analysis of most of the condensable products was done by gas-liquid chromatography (GLC). A Le Roy still (8) was occasionally used to separate the products from excess initial olefin. The hydrocarbon gases formed and carbon dioxide were analyzed mass spectrometrically after preliminary separation by GLC. Formic acid was determined qualitatively from infrared spectra of the products (using a gas cell 10 cm long) after removal of more volatile compounds on the Le Roy still and quantitatively by titrating with *N*/50 NaOH using phenolphthalein indicator. No quantitative determinations of formaldehyde were attempted because of its tendency to polymerize and consequently its difficult quantitative recovery from the reaction apparatus. In the case of some terminal olefins its presence was shown qualitatively by reaction with chromotropic acid and by the infrared spectra of the condensable products. On the whole, in most cases not too important quantities of formaldehyde appeared to be recovered.

The products eluted by GLC were collected in liquid nitrogen traps and their identity was confirmed by infrared and mass spectroscopy. The GLC arrangement was essentially as described previously (9) but with an internal capillary regulating the outlet pressure instead of an external leak. Two 1/4-in. I.D. columns were alternatively used: (1) a 40-ft tricresyl phosphate (TCP) on firebrick column (40 wt.% TCP) operated at 125°C, and (2) an 8-ft dinonylphthalate (DNP) on glass beads column (4 wt.% DNP) operated at room temperature. Helium was used as the carrier gas in both cases. Some separations of lighter gases (CO<sub>2</sub>, ethane, ethylene) were kindly made by Dr. N. F. Foster on a 40-ft dimethyl sulpholane (DMS) on firebrick column (40 wt.% DMS) operated at room temperature.

For comparison with the data obtained in the vapor phase the liquid-phase ozonization of ethylene, isobutene, and 1-butene was carried out at -78°C in ethylchloride solution in a separate series of experiments.

## RESULTS

The products of the reactions of ozone with a number of olefins in the vapor phase, as observed by the analytical procedures used in the present work, are shown in Table I. The quantities are expressed as molecules of products formed per molecule of ozone consumed.

It should be stressed that the quantities of the carbonyl compounds shown in Table I are based on GLC peak areas and are, therefore, the products observed *after* the condensables are passed through the GLC column and include any products of decomposition of the original compounds in the course of the analysis. This is, in particular, true of the initially present peroxides (shown qualitatively by a positive KI test, for example in the liquid products of isobutene, 1-butene, *cis*-2-pentene, and *trans*-2-pentene) which appear to be reduced to the corresponding carbonyl compounds. Thus in the case of isobutene

TABLE I  
Number of moles of products formed per 1 mole of ozone consumed

Olefin	Aldehydes										
	CO <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	HCOOH	CH <sub>3</sub> OH	MEK <sup>a</sup>	Ac <sup>b</sup>
C <sub>2</sub> H <sub>4</sub>	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.25	—	—	.019
C <sub>2</sub> H <sub>6</sub>	.32	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	.34	.033	—	.38
C <sub>3</sub> H <sub>6</sub>	.40	.031	.056	.002	—	n.d.	n.d.	.24	.014	—	.133
n-C <sub>4</sub> H <sub>10</sub> -1	.29	—	—	.046	.129	—	—	.20	—	—	.061
n-C <sub>4</sub> H <sub>10</sub> -1	.23	—	.005	tr.	—	.027	.076	.24	—	.015	.005
3(CH <sub>3</sub> )C <sub>4</sub> H <sub>7</sub> -1	.29	—	—	.081	.132	—	—	.25	.015	.074	.032
iso-C <sub>4</sub> H <sub>8</sub>	.37	—	—	.005	.009	—	tr.	.66	.013	.53	—
2(CH <sub>3</sub> )C <sub>4</sub> H <sub>7</sub> -1	.54	—	—	—	—	—	tr.	.33	.113	.42	.130
cis-C <sub>4</sub> H <sub>8</sub> -2	.42	—	—	.023	—	—	tr.	.20	.152	—	1.02
trans-C <sub>4</sub> H <sub>8</sub> -2	.35	—	—	.014	tr.	—	—	.23	pr.	—	1.06
cis-C <sub>4</sub> H <sub>10</sub> -2	.30	—	.014	—	—	—	—	.20	.013	—	.56
trans-C <sub>4</sub> H <sub>10</sub> -2	.36	.018	.096	.003	—	—	—	.16	.012	—	.56
C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> )H	.29	—	—	tr.	tr.	.026	—	.24	.058	.43	pr.
C(CH <sub>3</sub> ) <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub>	.40	—	—	tr.	—	—	—	.22	pr.	1.49	.010
Cyclohexene	.59	.118	—	—	—	—	—	.29	—	—	.014
Butadiene-1,3	.24	.114	—	.014	—	.004	.004	.18	—	—	.026
											.43

NOTE: n.d. = not determined; tr. = perhaps a trace present; pr. = qualitatively identified but not measured quantitatively. The meaning of the singly and doubly underlined figures and the figures in boldface type is explained in the text.

<sup>a</sup>MEK = methyl ethyl ketone. <sup>b</sup>Ac = CH<sub>3</sub>CHO. <sup>c</sup>Pr = C<sub>3</sub>H<sub>7</sub>CHO. <sup>d</sup>iso-Bu = iso-C<sub>4</sub>H<sub>9</sub>CHO. <sup>e</sup>MF = methyl formate.

<sup>f</sup>Isobutene produced also methyl acetate (.003) and *tert*-butanol (.009).



only a fraction (about 13%) of the total acetone was recovered from the liquid products on the Le Roy still at  $-75^{\circ}$ , at which temperature-free acetone should be recovered readily. Some other olefins seemed to show similar behavior but the amounts of the "free" and the "bound" carbonyl compounds were not determined separately.

Since in the present experiments large excess of the olefins was always used, it was not feasible in some cases to analyze for the reaction products of volatilities or GLC elution times similar to those of the olefins; thus the information obtained for the reaction with ethylene is very incomplete. In the case of 2-methyl-2-butene acetaldehyde could not be evaluated quantitatively by GLC analysis, although it was evidently formed in significant amounts as anticipated. Also, any compounds of very low volatility and long GLC elution times would not be readily detected. This is very probably responsible for the limited information on the products of the reaction of cyclohexene.

In order to test whether some double-bond isomerization may occur in the course of these reactions, the butene recovered from the reaction of excess *cis*-2-butene with ozone was analyzed by GLC and found not to have undergone any isomerization.

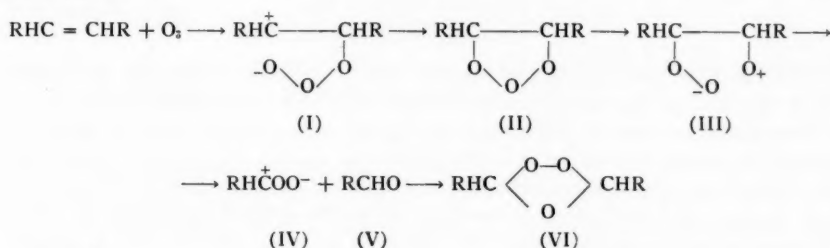
Liquid-phase ozonization of ethylene, isobutene, and 1-butene produced the expected ozonides in addition to minor amounts of degradation products (carbon dioxide, formaldehyde, formic acid). However, in the case of both isobutene and 1-butene small amounts of ethylene ozonide (about 10% of the main ozonide in each case) were also recovered by GLC analysis and its identity was confirmed by infrared spectroscopy (10). In addition, the GLC analysis showed about 20% of acetone in the case of isobutene and about 10% of propanal in the case of 1-butene, both apparently formed by degradation of the ozonide. In the case of isobutene, a fair amount of non-explosive crystals (melting point of the crude crystals  $91-95^{\circ}$ ) of peroxidic character (giving positive KI test) were isolated on leaving the reaction product stand overnight at room temperature.

#### DISCUSSION

Most of the previous investigations of the products of the reactions of ozone with olefins in the vapor phase have been recently reviewed by Leighton and Perkins (11). The present work agrees in its main outlines with the previous observations although there are also some differences between the results obtained by various workers. However, in comparing and assessing the results of such studies there are in particular two features of these processes which have to be kept in mind: (1) Appreciable quantities of relatively unstable intermediate peroxidic compounds are initially formed (12, 13) and the final stable products observed will depend on the conditions under which the degradation takes place. The particular analytical procedure used may therefore strongly affect the amounts and the type of the stable products observed. (2) The reactions are highly exothermic and the liberated heat is as a rule likely to affect their course, at least to some extent and sometimes very drastically, especially in the presence of large excess of molecular oxygen as is usually the case. Under conditions of the present experiments too rapid introduction of ozonized oxygen into the olefin vapor led, at least in some cases, to strong warming of the reaction vessel and GLC analysis then showed essentially only large amounts of  $\text{CO}_2$  and water in the products, indicating complete combustion. With slow introduction of the ozone-oxygen mixture no significant warming of the reaction vessel occurred and no water peak was observed by GLC although some  $\text{CO}_2$  was always formed, as shown in Table I and as observed in most of the previous work. Evidently, it is difficult to eliminate altogether quantitative uncertainties about the possible effect of "hot" products in these reactions.



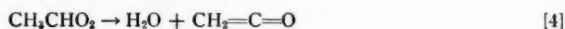
Substantial fractions of the products formed under the particular experimental conditions employed in the present work have been isolated in most cases and can be discussed briefly in terms of the generally accepted mechanism of ozone interaction with olefinic compounds. With some vagueness as to the exact detail, this mechanism can be written down as follows:



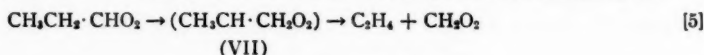
The initial addition may be a two-step process, as indicated above, in which case I could equally well be visualized as a  $\pi$ -complex (14). On the other hand, a one-step addition would lead directly to the "initial ozonide" (II), which is extremely unstable. Criegee has recently obtained evidence that the initial ozonide is formed at least under some conditions (15). He and his co-workers have also been responsible for the identification of IV as a relatively stable and long-lived zwitterion which can enter into reactions such as addition to an aldehyde (V) to form an ozonide (VI). At low temperatures in solution this last reaction is, no doubt, assisted by the solvent cage effect and usually predominates. At higher temperatures and in the vapor phase other competing reactions of the zwitterion (IV) become important and the process is then characterized by considerable complexity. The types of reactions which the zwitterion (IV) can undergo are of particular importance. These include dimerization and polymerization, with or without participation of water, into peroxidic substances; reactions with any reactive compounds present in sufficient concentration; rearrangement; and decomposition.

The presence of peroxidic intermediates in the products obtained in the present work was shown qualitatively. In the course of GLC analysis these appeared to decompose with the release of the "bound" carbonyl compounds. Some years ago Briner and co-workers isolated and at least partially characterized some of the peroxidic substances formed in the vapor phase olefin-ozone reactions (12, 13). Hydrolysis of these compounds led to the release of the "bound" carbonyl compounds and acids. In the case of 2-butenes and propylene, in addition to the predominant amounts of formic acid, they also observed after hydrolysis smaller quantities of acetic acid. Since, in our case, acids could not be observed directly by GLC analysis, infrared spectra were taken of the products before GLC analysis and in all cases only formic acid was found to be present. The values in Table I given as formic acid, however, have been obtained by titration and may also include any higher acids liberated on hydrolysis. Ozonides were not observed, although some of the more volatile ozonides (ethylene-, isobutene-, and 1-butene-ozonide) produced by low temperature ozonization in solution could be analyzed readily by GLC in spite of their relative instability. This is in agreement with the results of Hanst *et al.* (4), although these authors observed by the use of long path infrared spectroscopy the ozonide formation from some heavier olefins (1-pentene, 1-hexene, 3-heptene). However, less volatile ozonides would not be readily observed under conditions of our GLC analysis and no attempt was made to explore this analytical possibility further.

Decomposition of the zwitterion (IV) has been postulated to explain the formation of various light compounds in the ozonization products (3, 4), thus



Reaction [3] and its homologues can readily explain the major amounts of paraffins as well as of ethylene in the case of butadiene (shown doubly underlined in Table I), and of the substantial amount of carbon dioxide formed in our experiments. Together with these paraffins, olefins containing the same number of carbon atoms (shown singly underlined in Table I) are also formed, although in somewhat smaller amounts. The formation of these olefins could perhaps be visualized as resulting from rearrangement through hydrogen migration of the zwitterion (IV) followed by decomposition, for example,



where  $\text{CH}_2\text{O}_2$  may again be a zwitterion (IV) and undergo further reactions. Equally well, the olefin formation may be a consequence of a "peroxide-formate" rearrangement (16) followed by decomposition in a particular way. This type of rearrangement is known to occur under some conditions and has been frequently invoked to explain the "abnormal" products of ozonization of olefins, such as formic acid, methanol, etc.

The major carbonyl compounds are the "normal" products (shown in Table I in boldface type). Small amounts of aldehydes containing the same number of carbon atoms as the original olefins (acetaldehyde from  $\text{C}_2\text{H}_4$ , propanal from  $\text{C}_3\text{H}_6$ , *n*-butanal from 1- $\text{C}_4\text{H}_8$ , isobutyraldehyde from iso- $\text{C}_4\text{H}_8$ ) are occasionally formed, suggesting that perhaps some molecular oxygen splits off from the intermediate (III) and the remainder then rearranges to an aldehyde. However, the quantities of these compounds formed are very small. Much more important amounts are formed of the carbonyl compounds one and, to a lesser extent, two carbon atoms shorter than the "normal" carbonyl compounds. They are underlined in Table I and include, for example, acetaldehyde in the case of 1-butene (besides the "normal" carbonyl compound propanal), acetone in the case of 3-methyl-1-butene (besides the "normal" isobutyraldehyde), etc. This degradation could again be visualized as being induced by "peroxide-formate" rearrangement although other mechanisms could be postulated as well, such as for example secondary oxidation or cyclization followed by decomposition of the rearranged intermediate (VII).

In view of the uncertainties mentioned at the beginning of this discussion and because of the analytical limitations, in particular lack of information on the exact nature of the intermediate peroxidic substances, a subject currently receiving considerable attention (17), and on the amounts of formaldehyde and non-condensable products ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CH}_4$ ) formed, the present results evidently provide only a limited picture of these complex vapor phase reactions. However, a preliminary broad survey has been made for a number of olefins under comparable conditions and it is hoped that the information obtained may supplement the observations of other workers made with the use of different analytical techniques and, in particular, help in the planning of more extensive future studies of selected individual reactions.

The products obtained in the low temperature ozonization in solution agree with the results of previous workers. However, it is of interest that in the case of 1-butene and

isobutene appreciable amounts of ethylene ozonide were isolated by GLC in addition to the expected ozonides of these two olefins. The formation of ethylene ozonide, in spite of some hindrance because of the solvent cage effect and the statistical probability favoring the formation of the unsymmetrical ozonides, seems to indicate that in the initial ozonides (II) of these two olefins the ring opening is not exclusively one way.

#### ACKNOWLEDGMENTS

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# CIS AND TRANS 1-ACETOXY-1,3-BUTADIENE: PHYSICAL AND CHEMICAL PROPERTIES, INFRARED AND ULTRAVIOLET SPECTRA<sup>1</sup>

K. K. GEORGIEFF AND A. DUPRÉ

## ABSTRACT

1-Acetoxy-1,3-butadiene was prepared by the reaction of crotonaldehyde with acetic anhydride in the presence of potassium or sodium acetate. The product was found to consist of two forms which, from their physical properties and infrared spectra, appear to be *cis* and *trans*. Mass and ultraviolet spectra, and methods of analysis are also reported. The *cis* form was found to be a substantially stronger inhibitor than the *trans* in the bulk polymerization of vinyl acetate using benzoyl peroxide as catalyst.

## INTRODUCTION

In a recent investigation on the inhibitory effect of various compounds on the rate of polymerization of vinyl acetate (which will be reported elsewhere), some unexpected results were obtained. 1-Acetoxy-1,3-butadiene was prepared from crotonaldehyde and acetic anhydride using potassium or sodium acetate as catalyst (1, 2). On distillation, a series of fractions were obtained with gradually changing boiling points, freezing points, refractive indices, specific gravity, and inhibitory effect on the bulk polymerization of vinyl acetate. To try to establish the reason for these differences, mass, infrared, and ultraviolet spectra were obtained.

## EXPERIMENTAL

### *Preparation of 1-Acetoxy-1,3-butadiene*

A modification of the method of Wacker (1) was used. A 240-g quantity of potassium acetate (Mallinckrodt analytical reagent) was charged into a 3-liter round-bottom flask fitted with a Tru-Bore stirrer, a feeding funnel, and a reflux condenser. The apparatus was evacuated and filled with nitrogen. Acetic anhydride (Shawinigan Chemicals Ltd., commercial grade) (440 g) was added and the mixture refluxed. Crotonaldehyde (Shawinigan Chemicals Ltd., redistilled) (240 g) was added drop-wise over a period of 3 hours and the mixture refluxed for an additional 20 minutes. The reaction mixture was cooled and shaken with 1200 cc of water. The organic layer was extracted first with just enough 10% sodium carbonate solution to neutralize the acetic acid, then with 1 liter of 40% sodium bisulphite solution, and finally with 200–300 cc of 10% sodium carbonate solution. After each extraction, the spent aqueous layer was extracted with 100–200 cc of ether and the ether layer added to the crude product. The crude product was dried with anhydrous sodium sulphate, stabilized with 2 g of para-tertiary butylcatechol and 2.5 g of copper resinate, and distilled in a copper column (3 ft long and 1 in. I.D.) packed with  $\frac{1}{4}$ -in. copper rings. The ether was distilled at atmospheric pressure and the product at 3 mm Hg absolute. Yield based on croton was about 60% and the conversion 50%.

The product was analyzed by saponification, reaction with dodecyl mercaptan (3), and bromination (4). Saponification was carried out in the presence of an excess of aqueous *N*/10 sodium hydroxide solution for 2 hours at room temperature. Results were 101–104% of theory. Analysis by the dodecyl mercaptan method using a reaction time of 2 minutes gave values from 95 to 99.9% based on the reaction with both double

<sup>1</sup>Manuscript received February 26, 1960.

Contribution from the Research Laboratories, Shawinigan Chemicals Ltd., Shawinigan Falls, Que.

bonds. Bromination with an aqueous mixture of bromine, sodium bromide, hydrochloric acid, and methanol for 30–60 minutes gave results of about 99%, based on the reaction with one double bond.

The inhibitory effect of 1-acetoxy-1,3-butadiene on the rate of the bulk polymerization of vinyl acetate was determined by a modification of a method previously used (5). The open flame heating was replaced by a Glas-Col mantle in order to increase reproducibility. Inhibition factors, which have been arbitrarily defined as the number of seconds by which pure vinyl acetate is made less active by 1 p.p.m. of inhibitor, were determined. Further details on this phase will be reported elsewhere.

Ultraviolet spectra were obtained with a Beckman DK-2 instrument using 1-cm cells. Infrared spectra were obtained with a Perkin-Elmer 12-C single-beam spectrometer having a sodium chloride prism and the mass spectra with a 60° Nier type instrument using 50 electron volts.

### RESULTS

The product was distilled into three fractions and each fraction redistilled into three or four fractions using a 6-ft column, 1 in. in diameter, packed with  $\frac{1}{4}$ -in. Berl saddles. In Table I will be found the data for that series of final fractions which was most completely studied.

TABLE I  
Properties of a series of fractions of 1-acetoxy-1,3-butadiene

Fr. No.	B.p. (uncorr.) at 32 mm abs.	$d_4^{20}$	$n_D^{20}$	M.p.	Analysis		Inhibition of vinyl acetate, sec/ p.p.m.	Ultraviolet spectrum	
					By sapon., %	By merc., %		$\lambda_{max}$ , m $\mu$	$\epsilon_{max}$
1*	53.2–54.2	0.949		Below $-78^\circ$	101.3	96.0	2.00	233.8	26,000
2	54.2–54.6	0.948	1.4647	Below $-78^\circ$	104.0	99.9	1.98	233.8	26,100
3	54.6–55.0	0.947		Below $-78^\circ$	102.9	99.1	1.88	233.4	26,500
4*	55.0–55.3	0.948	1.4703	$\sim -55$ to $-60^\circ$	102.0	95.3	1.68	233.2	26,000

\*Contained trace of water.

To try to establish the reason for the differences between fractions as given in Table I, mass spectra were first obtained. There was no indication of the presence of substantial amounts of impurities. The parent peak had a mass of 112 and the base peak 43. All the major peaks could be justified on the basis of the 1-acetoxy-1,3-butadiene structure. Further confirmation of the molecular weight (i.e. 112) was obtained from the analyses (i.e. saponification, reaction with dodecyl mercaptan, and bromination).

The reaction of both double bonds in 1-acetoxy-1,3-butadiene with dodecyl mercaptan did not always go to 100% completion. Doubling the amount of potassium hydroxide catalyst and the duration of reaction made no difference to the results in the one fraction studied. However, the values were sufficiently high to establish clearly the presence of two double bonds. On the other hand, only one double bond brominated in aqueous medium but the reaction was very close to quantitative and can be used as a method of analysis.

Further evidence of the structure was obtained from the ultraviolet spectrum (cf. Fig. 1 and Table I). Both the wave length and the molar extinction coefficient were

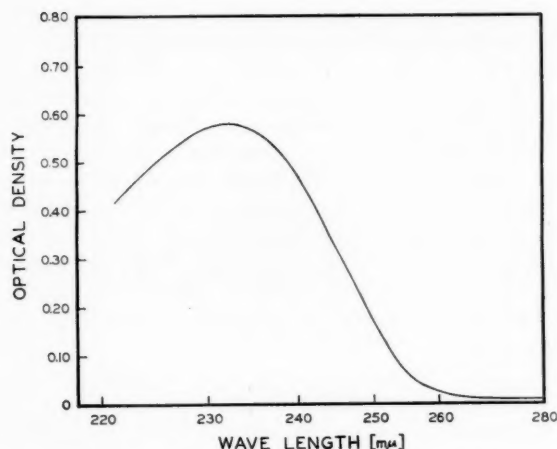


FIG. 1. Ultraviolet absorption spectrum of *cis* and *trans* 1-acetoxy-1,3-butadiene.

close to the values expected for the 1,3-butadiene structure. A 1,2- or 2,3-butadiene, on the other hand, would have been expected to absorb at lower wave lengths and have a much lower extinction coefficient.

A study of the data in Table I suggested the presence of at least two forms of 1-acetoxy-1,3-butadiene and therefore one attempt was made to make a separation by gas chromatography. This was unsuccessful although a shoulder on the main band was obtained. This is in direct contrast to the ease with which 1-acetoxy-1,3-butadiene was separated from 2-acetoxy-1,3-butadiene. It was thus apparent that the two or more forms present were more closely related than position isomers and hence *cis-trans* isomerism was suspected. In most, if not all, compounds the *cis* form melts at a lower temperature than



the *trans*. It was, therefore, surmised that the lowest boiling fraction (fraction No. 1) was predominately *cis* while the highest boiling (fraction No. 4) was chiefly *trans*. This was confirmed by the infrared spectra which are given in Fig. 2. Wave lengths of the bands are given in Table II.

In compounds of the form  $\text{R}_1\text{CO.OCH}=\text{CHR}_2$  the expected position of the carbonyl band in the infrared is at about  $1770 \text{ cm}^{-1}$  (6, 7, 8, 9, 10). In all of our fractions the band was at  $1763 \text{ cm}^{-1}$ . The possibility of having a compound of the form  $\text{R}_1\text{CH}=\text{CH.COOR}_2$  which has a carbonyl absorption at about  $1720 \text{ cm}^{-1}$  was clearly eliminated (6, 7, 8, 11). The C—O stretching vibrations of carboxylic esters of the form  $\text{CH}_3\text{CO.OCH}=\text{CHR}$  give strong bands between  $1218$  and  $1204 \text{ cm}^{-1}$  and between  $1159$  and  $1096 \text{ cm}^{-1}$  (6, 12, 13). These bands are usually accompanied by weak bands between  $1300$  and  $1000 \text{ cm}^{-1}$ . An examination of our spectra shows definitely these characteristic bands. The terminal methylene group undoubtedly gives rise to the band at  $1375 \text{ cm}^{-1}$  while



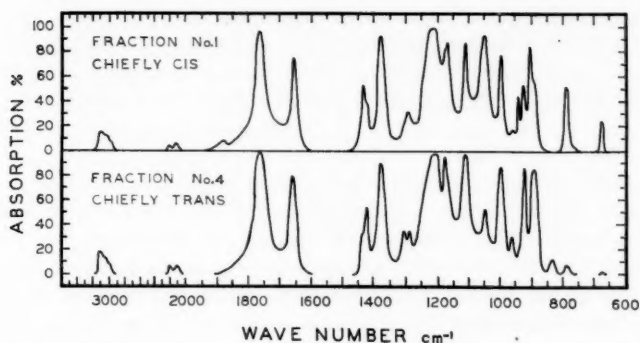


FIG. 2. Infrared absorption spectra of cis and trans 1-acetoxy-1,3-butadiene 5% solution in  $\text{CCl}_4$  or  $\text{CS}_2$ , 0.121-mm cell.

TABLE II  
Infrared bands of trans and cis 1-acetoxy-1,3-butadiene

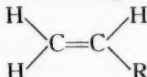
Fr. IV, trans	Fr. I, cis	Remarks
3102W	3102W	
3052VW	3042VW	Shift
3008VW	3000VW	Shift
2210VW	2210VW	
2100VW	2115VW	Shift
	1878VW	
1763S	1763S	Stronger in trans than in cis
1659M	1656M	Shift
1423M	1432M	Shift
1375S	1375S	
1307W		
1289W	1291W	Shift
1209VS	1213VS	
1178S	1172M	Shift and stronger in trans
1111S		Characteristic
	1049S	Characteristic
998S	998S	Stronger in trans than in cis
959W		Characteristic
	941M	Characteristic
924S		Characteristic
	907S	Characteristic
893S		Characteristic
835W		Characteristic
	788M	Characteristic
	675W	Characteristic

NOTE: The bands that are believed to be due to mutual contamination have been omitted.

the terminal methyl gives a band at  $1432\text{ cm}^{-1}$  in fraction No. 1 and at  $1423\text{ cm}^{-1}$  in fraction No. 4. The infrared spectrum would, therefore, appear to be consistent with a 1-acetoxy-1,3-butadiene structure.

The following infrared data confirm the previous indication of cis-trans isomerism. The intensity of the carbonyl band in esters has been found by Allan, Meakins, and Whiting (14) to vary with the nature of the unsaturated bond but is stronger in the trans compound than in the cis. In our product, the carbonyl band in fraction No. 4 was stronger than that in fraction No. 1. Therefore, fraction No. 4 would be expected to be predominantly trans and fraction No. 1 chiefly cis. Furthermore, conversion of

the  $\alpha,\beta$ -ethylenic bond from trans to cis has been found by the same authors (14) to cause a shift of the C=C stretching bond to lower frequency. The bands in our fraction No. 4 were found to be at higher frequencies than those in fraction No. 1. The terminal C=C of the form



about 990 and about 910  $\text{cm}^{-1}$ , the latter being three times the intensity of the former (6). In our fraction No. 4 (trans), two bands at 998 and 893  $\text{cm}^{-1}$  are observed, the relative intensities being as previously stated. In the case of fraction No. 1 (cis), bands are observed at 998 and 907  $\text{cm}^{-1}$  although the intensity of the latter is about the same order of magnitude as the former. However, this irregularity is often observed in the cis form. It has been noted that the spectrum of the cis is usually weaker than the trans. The  $\alpha,\beta$ -ethylenic group, which gives rise to the cis-trans isomerism, is expected to give bands between 990 and 910  $\text{cm}^{-1}$ . In fraction No. 4 (trans), the bands at 924 and 959  $\text{cm}^{-1}$  are undoubtedly due to this group. In fraction No. 1 (cis), the band at 941 and possibly the ones at 788 and 675  $\text{cm}^{-1}$  can be attributed to this unsaturation. The bands due to cis isomerism have not been rigorously established in the literature.

Only one band was observed due to C=C stretching, i.e. at 1659  $\text{cm}^{-1}$  (trans) and 1656  $\text{cm}^{-1}$  (cis). Another one at about 1640  $\text{cm}^{-1}$  was expected. This suggests that the two C=C groups are not in the same plane (15).

Further confirmation of the cis and trans assignments was made from the nuclear magnetic resonance spectra (16) by Bernstein (National Research Council, Ottawa). Agreement with the infrared data was near quantitative for mixtures of the two forms.

From the data in Table I, it is obvious that the cis form (fraction No. 1) is a stronger inhibitor than the trans (fraction No. 4) for the bulk polymerization of vinyl acetate using benzoyl peroxide as catalyst. In all the distillation fractions studied, the highest inhibition factor obtained was 2.02 seconds per p.p.m. (cis) and the lowest 1.55 (trans). Inhibition factors for the total product were found to vary somewhat from run to run, e.g. with sodium acetate as catalyst 1.79 and 1.87 and with potassium acetate 1.87. However, sufficient work was not done to establish which factors influenced the proportion of the two forms produced.

#### ACKNOWLEDGMENTS

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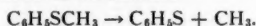
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# THE THERMAL DECOMPOSITION OF PHENYL METHYL SULPHIDE<sup>1</sup>

MARGARET H. BACK<sup>2</sup> AND A. H. SEHON

## ABSTRACT

The thermal decomposition of phenyl methyl sulphide was investigated in a flow system in an excess of toluene. The main products were methane, thiophenol, and dibenzyl. The primary mode of decomposition was ascribed to the reaction



The rate constant for this process was given by the expression

$$k = 3 \times 10^{14} \cdot e^{-80,000/RT} \text{ sec}^{-1}$$

## INTRODUCTION

The benzyl radical has long been known to be fairly stable thermally and relatively unreactive (1, 2). These properties have been attributed to its conjugated structure which allows the free electron to be largely delocalized (3, 4). Radicals with structures similar to that of the benzyl radical might also be expected to be stabilized by resonance and hence to form relatively weak bonds with other radicals. It was anticipated that the phenylsulphide radical,  $\text{C}_6\text{H}_5\text{S}$ , satisfies these conditions. To test this hypothesis the kinetics of the thermal decomposition of phenyl methyl sulphide in a stream of toluene was studied.

## EXPERIMENTAL

### Materials

Phenyl methyl sulphide was kindly supplied by Dr. W. L. Hawkins of Bell Telephone Laboratories, N.J., and was further purified by distillation at low pressure. Toluene was generously supplied by Gulf Oil Corporation, Pittsburgh, Pa., and was purified by distillation through an efficient column. The fraction boiling at 110.5° C was used in this study.

### Apparatus

The pyrolysis was studied in a conventional vacuum flow system similar to those employed in previous investigations using the toluene carrier technique (5). The toluene pressure was varied between 5.7 and 10.1 mm Hg. Weighed amounts of the sulphide were admitted from a small detachable vial through a short capillary which led into the toluene stream. The vapor pressure of the sulphide could be changed by heating the vial to different temperatures with a removable bath containing dibutylphthalate. The temperature of the bath was varied between 80° C and 96° C, giving a partial pressure of sulphide from 0.5% to 2% of the toluene pressure. The decomposition was studied over the temperature range 550° C to 706° C.

### Analysis

The products were condensed in a series of three traps maintained at -5° C, -78° C, and -188° C. The material collected in the first trap was weighed and analyzed for disulphide according to the procedure outlined by Kolthoff (6). The contents of the trap maintained at -78° C were titrated for mercaptan with 0.1 N silver nitrate solution,

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using a rotating platinum electrode and a microammeter (7). The method was calibrated with thiophenol solution of known concentrations. Some titrations were also done potentiometrically with a silver wire electrode (8). The two methods of titration gave identical results and the former method was generally used. Non-condensable gases were pumped into calibrated bulbs with the aid of two diffusion pumps connected in series and were analyzed by combustion on copper oxide at 300° C.

## RESULTS AND DISCUSSION

*Products*

The main products of the decomposition, shown in Table I, were methane and a mercaptan, which was considered to be thiophenol. The ratio of mercaptan to methane varied from 1.1 to 1.6, increasing with increasing temperature. Methane accounted for 90 to 96% of the non-condensable gases and the remainder was hydrogen.

TABLE I  
Products of the decomposition of phenyl methyl sulphide

Expt. No.	T, °A	Toluene pressure,		Non- cond. gases, P <sub>s</sub> /P <sub>t</sub> * mmoles	CH <sub>4</sub> , %	H <sub>2</sub> , %	CH <sub>4</sub> , mmoles	SH <sup>-</sup> , mmoles	Dibenzyl, mmoles	SH <sup>-</sup> , CH <sub>4</sub>	Dibenzyl, CH <sub>4</sub>	%	k, sec <sup>-1</sup>	k', sec <sup>-1</sup>
		t, sec	mm Hg									decomp.		
33	823	.56	12.15	.0435	93.4	6.6	.0387					5.2	.068	.025
8	842	.79	10.9	.014	.0682	94.1	5.9	.0616	.078	.033	1.27	.54	5.2	.068
9	842	.79	12.3	.005	.0624	91.8	8.2	.0538	.068		1.26		5.2	.066
7	852.5	.66	10.9	.015	.0699	94.5	5.5	.0635		.043		.68		.084
27	857	.32	10.5	.0064	.0598	92.8	7.2	.0527	.060	.023	1.14	.44	3.8	.121
28	858	.34	10.3	.013	.0696	94.5	5.6	.0632		.046		.73		.098
30	870	.44	5.1	.009	.1053	95.6	4.3	.0978		.084		.86		.159
31	870	.34	11.4	.010	.0853	95.0	5.0	.0782						.168
26	880.5	.32	9.9	.0085	.1046	94.6	5.4	.0953	.125	.061	1.31	.64	9.9	.326
10	882.5	.66	10.5	.015	.218	95.5	4.6	.201	.273	.167	1.36	.83	20.2	.348
2	883	.61	9.9	.032	.1478	94.5	5.5	.134	.184	.129	1.37	.96	16.0	.283
3	883	.62	10.1	.005	.188	94.5	5.5	.171	.207	.114	1.21	.61	18.3	.328
32	891.5	.38	11.6	.012	.1560	95.2	4.8	.1437						.351
25	904	.32	10.15	.0073	.220	95.4	4.7	.203	.28	.180	1.38	.89	24.8	.891
29	905	.31	10.1	.0075	.225	95.5	4.5	.208	.300	.18	1.44	.87	25.0	.916
6	906	.61	10.0	.023	.292	92.8	7.2	.258	.370	.240	1.43	.93	36.4	.740
12	907	.78	5.8	.015	.370	94.8	5.2	.337	.512	.31	1.52	.92	47.6	.821
4	922	.58	10.1	.018	.470	92.0	8.0	.407	.591	.374	1.45	.92	58.2	1.49
5	923	.60	10.2	.0068	.597	95.2	4.8	.549	.767	.517	1.40	.94	67.5	1.86
14	923	.76	5.7	.0145	.514	93.5	6.5	.458	.723		1.58	.79	67.2	1.47
24	934.5	.32	10.4	.007	.455	94.6	5.4	.414	.580	.360	1.40	.87	55.9	2.53
23	951	.29	10.1	.008	.519	93.9	6.1	.466		.41		.88		2.12
21	979	.28	10.2	.0074	.418	90.4	9.6	.351	.560	.32	1.60	.91	89.9	8.29
22	979	.27	10.4	.007	.444	90.1	9.8	.371	.542	.33	1.46	.89	82.2	6.31

\*P<sub>s</sub> and P<sub>t</sub> refer to the partial pressures of phenyl methyl sulphide and toluene, respectively.

No disulphide was detected in the trap maintained at -5° C. The product collected in this trap was shown to be dibenzyl. Neither ethane nor methyl mercaptan were detected among the products.

*Mechanism of Decomposition*

The results suggested that the primary step in the pyrolysis of phenyl methyl sulphide involved the dissociation of the C—S bond,



and that the phenylsulphide and methyl radicals formed reacted further with toluene to form thiophenol and methane,



In addition, the benzyl radicals formed in reactions [2] and [3] recombined, at least in part, to give dibenzyl.

According to this mechanism thiophenol, methane, and dibenzyl would be formed in equimolar amounts. However, the yield of methane was always less than that of the mercaptan, this discrepancy becoming more pronounced with increasing temperature. Furthermore, the amount of dibenzyl formed was found to be slightly less than the yield of methane. Therefore, reactions [1], [2], [3], and the dimerization of benzyl radicals do not fully represent the mechanism of the decomposition.

These findings may be explained by postulating that methyl radicals may not react sufficiently rapidly with toluene in the temperature range of the decomposition, 550° C to 706° C, to be quantitatively converted to methane. Similar conclusions were reached by Szwarc and Taylor (9), who showed that at 780° C about 25% of the methyl radicals produced in the thermal decomposition of acetone in a stream of toluene were removed by recombination with benzyl radicals,



and about 1 to 2% by dimerization,



rather than by reaction with toluene. In the present study no ethane was detected among the products; however, its rate of production would be expected to be much less than that of ethylbenzene, because the steady-state concentration of benzyl radicals is probably much greater than that of methyl radicals.

With increase in temperature, the rate of reaction [4] would be expected to increase more rapidly than the rate of reaction [3]. This trend was indeed observed as evidenced by the increase in the ratio of thiophenol to methane with increasing temperature.

If reactions [1] to [4] occurred, the yield of dibenzyl should equal that of methane. The ratio of dibenzyl to methane was usually between 0.70 and 0.95, and it is suggested that losses of the dibenzyl due to inefficient trapping could account for the deviation of these values from unity (10).

The first-order rate constants for the decomposition of phenyl methyl sulphide were calculated from the rates of formation of methane and thiophenol, and are given in Table I. The rate constant for the production of methane,  $k'$ , was always less than that for the production of thiophenol,  $k$ . The plots of  $\log k$  and  $\log k'$  against  $1/T$  are shown in Fig. 1. Both curves deviate from linearity at high temperatures, but the drop in  $k'$  is more pronounced than that in  $k$ . The effect of changes in contact time, partial pressures of phenyl methyl sulphide and toluene are shown in Tables II, III, and IV, respectively. These results suggest that the decomposition of phenyl methyl sulphide may be considered to be a first-order process.

The extent of reaction [3] may, with certain assumptions, be calculated. The concentration of benzyl radicals may be estimated if it is assumed that there is little recombination in the hot zone. As a first approximation, the total production of benzyl radicals will then be equal to the sum of the thiophenol and methane produced less the amount



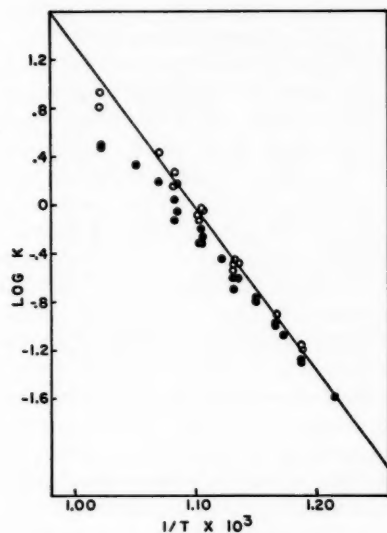


FIG. 1. Plot of  $\log k$  against  $1/T$  for the thermal decomposition of phenyl methyl sulphide. O calculated from the production of thiophenol ( $k$ ). ● calculated from the production of methane ( $k'$ ).

TABLE II  
Effect of reaction time on  $k$

Expt. No	$T, ^\circ\text{A}$	$t, \text{sec}$	$k, \text{sec}^{-1}$
26	880.5	.31	.326
3	883	.62	.328
29	905	.31	.916
12	907	.78	.821

TABLE III  
Effect of pressure of phenyl methyl sulphide on  $k$

Expt. No.	$T, ^\circ\text{A}$	Phenyl methyl sulphide, mm Hg	$k, \text{sec}^{-1}$
9	842	.06	.066
8	842	.15	.068
3	883	.05	.328
10	882.5	.17	.348
2	883	.32	.283

removed by recombination with methyl radicals. The latter quantity may be taken as the difference between the thiophenol and methane formed. Thus, the total production of benzyl radicals is equal to twice the production of methane, and its average yield may be considered as one half of this quantity. Assuming that the concentration of methyl

TABLE IV  
Effect of toluene pressure on  $k$

Expt. No.	$T, ^\circ\text{A}$	Toluene pressure, mm Hg	$k, \text{sec}^{-1}$
12	907	5.8	.821
6	906	10.0	.740
14	923	.57	1.47
4	922	1.01	1.49

radicals is stationary, the rate of production of methane is given by the following equation:

$$\frac{d(\text{CH}_4)}{dt} = \frac{k_1 k_3 (\text{C}_6\text{H}_5\text{SCH}_3)(\text{C}_6\text{H}_5\text{CH}_2)}{k_3 (\text{C}_6\text{H}_5\text{CH}_3) + k_4 (\text{C}_6\text{H}_5\text{CH}_2)}$$

The rate constant for the reaction of methyl radicals with toluene,  $k_3$ , has been measured by Trotman-Dickenson and Steacie (11), who found  $k_3 = 1.4 \times 10^{11} \cdot e^{-8300/RT}$  mole<sup>-1</sup> cc sec<sup>-1</sup>. The rate of production of thiophenol was taken as a measure of the rate of reaction [1], i.e.,  $k_1$  was taken equal to  $k$ . The production of methane for any particular experiment may then be calculated if a value is assumed for the rate constant,  $k_4$ , for the recombination of benzyl and methyl radicals. In a similar calculation Szwarc and Taylor (9) took this rate constant to be  $10^{12}$  mole<sup>-1</sup> cc sec<sup>-1</sup>, which is slightly less than the value for the recombination of methyl radicals. With these values the yield of methane was calculated for eight experiments, and the results were compared with the observed yields of methane (Table V).

TABLE V  
Calculated and observed yields of methane

Expt. No.	$T, ^\circ\text{A}$	Yield $\text{CH}_4$ , mmoles	
		Calc.	Obs.
9	842	.055	.054
27	857	.050	.053
26	880.5	.088	.095
25	904	.164	.203
29	905	.179	.208
4	922	.156	.407
5	923	.375	.549
24	934.5	.308	.414

The agreement between the observed and calculated values is better than could be expected in view of the approximations made and the uncertainty in the values  $k_3$  and  $k_4$ , and suggests that under the conditions of the experiments methyl radicals were not completely scavenged by toluene and that some reacted with benzyl radicals to give ethylbenzene. However, at the higher temperatures some of the ethylbenzene would be decomposed to give methyl radicals\* and, therefore, one would expect, as actually

\*The activation energy and the frequency factor for the decomposition of ethylbenzene are 3 kcal/mole greater than and 10 times less than the corresponding parameters for the decomposition of phenyl methyl sulphide. Therefore, the rate constant for the decomposition of ethylbenzene is considerably less than that for phenyl methyl sulphide and was neglected in the calculation of the concentration of methyl radicals.

observed, an increase in the production of methane at the higher temperatures relative to the calculated values.

If recombination reactions of the phenylsulphide radical occurred, the rate constant for the production of thiophenol,  $k$ , would be expected to fall as the temperature was increased. The Arrhenius plot exhibited in fact some deviation from linearity, but only at the highest temperature attained. Thus, it would appear that phenylsulphide radicals, unlike methyl radicals, were efficiently scavenged by toluene. This seems plausible because the possible recombination products of the phenyl sulphide radical, i.e. diphenyldisulphide or phenylbenzyl sulphide, would probably not be sufficiently stable and would, therefore, not be formed in the hot reaction zone. In consequence one may consider the phenyl radicals to be removed only in reaction [2] with toluene and one may conclude that, in the region where the plot of  $\log k$  vs.  $1/T$  is linear, the rate of production of thiophenol is to a good approximation a measure of the rate of decomposition of phenyl methyl sulphide into phenylsulphide and methyl radicals. The activation energy and frequency factor calculated from the linear portion of the plot were 60 kcal/mole and  $3 \times 10^{14}$  sec<sup>-1</sup>, respectively.

The effect of the surface of the reaction vessel on the decomposition was not investigated and, therefore, the activation energy of 60 kcal/mole may be only tentatively identified with the dissociation energy of the  $C_6H_5S-CH_3$  bond. A value of 73 kcal/mole was suggested by Franklin and Lumpkin (12) for  $D(CH_3S-CH_3)$  on the basis of their results obtained with the electron impact method. The difference between  $D(CH_3S-CH_3)$  and  $D(C_6H_5S-CH_3)$ , which may amount to 13 kcal/mole, represents then the difference in resonance energies of the methylsulphide and the phenylsulphide radicals. Hence, the actual value of the resonance energy of the phenylsulphide radical would be at least 13 kcal/mole.

#### ACKNOWLEDGMENTS

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## THE SYNTHESIS OF SOME BASIC ESTERS OF 3,4,5-TRIMETHOXYBENZOIC ACID<sup>1</sup>

GERASSIMOS FRANGATOS, GEZA KOHAN, AND FRANCIS L. CHUBB

### ABSTRACT

A series of basic esters of 3,4,5-trimethoxybenzoic acid was obtained from the reaction of 2-chloroethyl and 3-chloropropyl 3,4,5-trimethoxybenzoate with secondary amines including 1,2,3,4-tetrahydro- $\beta$ -carboline. The latter compound was prepared by the lithium aluminum hydride reduction of 1,2,3,4-tetrahydro-1-oxo- $\beta$ -carboline.

The remarkable effect of reserpine on the central nervous system has resulted in a wide application of this alkaloid primarily in states of hypertension and anxiety. However, the serious side effects of the drug and its high cost made it desirable to explore synthetic routes for the preparation of moieties which would retain the desirable pharmacodynamic properties with lesser or no interference from adverse side reactions. Miller and Weinberg (1), in view of the fact that the presence of the 3,4,5-trimethoxybenzoyl group in the reserpine molecule was necessary for its activity, prepared a number of basic esters of 3,4,5-trimethoxybenzoic acid. They reported reserpine-like activity for some of these compounds, especially those which contain three carbon atoms between the nitrogen and the ester group. This observation stimulated the synthesis and pharmacological testing of compounds of this type. Vejdělek (2), Supniewski (3), Sastry and Lasslo (4), Shapiro (5), Latus and Combes (6), and Solov'ev (7) have synthesized a number of basic esters by bringing about the esterification of an aminoalcohol with 3,4,5-trimethoxybenzoyl chloride.

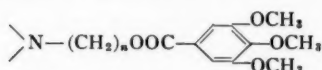
This communication reports some of the work done in these laboratories in which another route to the synthesis of basic esters was followed. The esters of halogenated alcohols with 3,4,5-trimethoxybenzoic acid were prepared and subsequently used as the alkylating agents in a series of secondary amines including 1,2,3,4-tetrahydro- $\beta$ -carboline. This method is especially advantageous in cases where the aminoalcohol is not readily available. The reaction was carried out with or without solvent usually in the presence of an acid acceptor such as  $K_2CO_3$ . In this case 2-chloroethyl 3,4,5-trimethoxybenzoate (I) and 3-chloropropyl 3,4,5-trimethoxybenzoate (II), prepared from 3,4,5-trimethoxybenzoyl chloride and the corresponding alcohol, were used as alkylating agents. The basic esters (III) prepared are listed in Table I. The reaction sequence is shown below.

1,2,3,4-Tetrahydro- $\beta$ -carboline (IV) was prepared from 1,2,3,4-tetrahydro-1-oxo- $\beta$ -carboline (V). The latter compound was prepared by applying a modification (8) of the procedure of Abramovitch and Shapiro (9). These authors have cyclized 2,3-dioxopiperidine-3-phenylhydrazine (VI) to V by using polyphosphoric acid or formic acid as acidic catalyst. This method had its limitations for it could not be used for relatively large scale operations due to the extensive polymerization and tar formation which occurred. However, when a mixture of concentrated hydrochloric acid and acetic acid was used the cyclization of VI to V proceeded in a satisfactory manner.

<sup>1</sup>Manuscript received March 14, 1960.

Contribution from the Research Laboratories, Frank W. Horner Limited, Montreal, Que.

TABLE I  
Basic esters of 3,4,5-trimethoxybenzoic acid

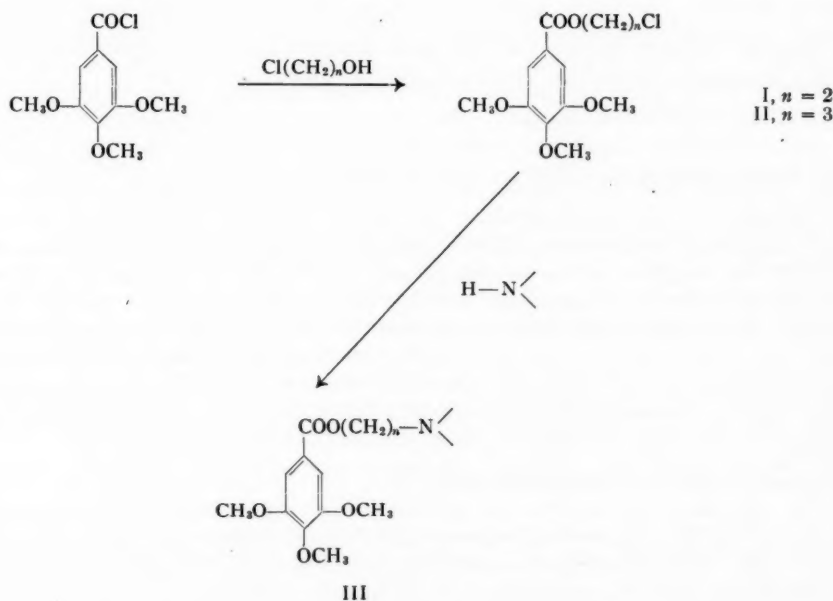


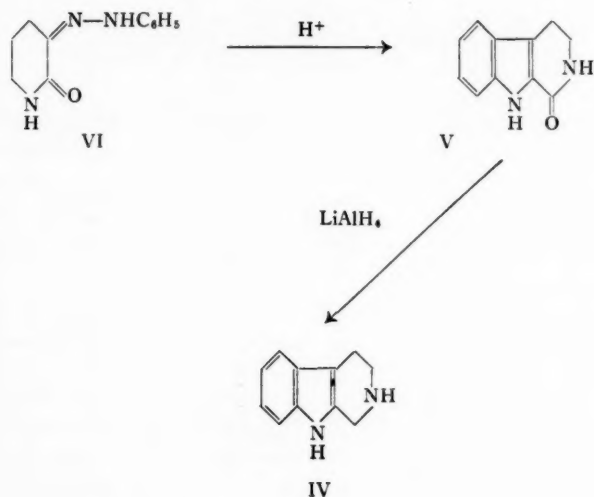
No.	N	n	Yield, %	Derivative	M.p.	Formula	Analyses					
							Calculated, %			Found, %		
							C	H	N	C	H	N
1 <sup>a</sup>	Morpholine	2	69.2	Hydrochloride	213°	C <sub>14</sub> H <sub>14</sub> ClNO <sub>4</sub>	53.11	6.63	3.87	52.98	6.62	4.00
				Picrate	178°	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>13</sub>	47.65	4.69	10.10	47.95	4.89	9.85
2	Morpholine	3	61.2	Hydrochloride	174°	C <sub>17</sub> H <sub>18</sub> ClNO <sub>4</sub>	54.32	6.92	3.43	54.07	7.08	3.79
3	Piperidine	2	72.3	Hydrochloride	210°	C <sub>17</sub> H <sub>18</sub> ClNO <sub>4</sub>	56.75	7.23	3.89	56.92	7.48	4.07
				Picrate	165°	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>13</sub>	50.00	5.07	10.14	49.91	5.22	10.51
4	Piperidine	3	68.3	Hydrochloride	168°	C <sub>18</sub> H <sub>18</sub> ClNO <sub>4</sub>	57.83	7.49	3.74	57.24	7.56	3.72
5	Pyrrolidine	2	53.6	Hydrochloride	182°	C <sub>14</sub> H <sub>14</sub> ClNO <sub>4</sub>	55.57	6.94	4.05	55.31	6.96	4.57
				Picrate	163°	C <sub>17</sub> H <sub>14</sub> N <sub>2</sub> O <sub>13</sub>	49.07	4.85	10.41	48.93	4.80	10.88
6	Pyrrolidine	3	55.6	Hydrochloride	154°	C <sub>17</sub> H <sub>18</sub> ClNO <sub>4</sub>	56.74	7.23	3.89	56.47	7.24	3.93
7 <sup>b</sup>	Diethylamine	2	54.8	Hydrochloride	159°	C <sub>16</sub> H <sub>18</sub> ClNO <sub>4</sub>	55.25	7.48	4.02	54.95	7.52	4.32
				Picrate	146°	C <sub>18</sub> H <sub>18</sub> N <sub>2</sub> O <sub>13</sub>	48.89	5.18	10.37	48.41	5.18	10.54
8 <sup>c</sup>	Diethylamine	3	47.0	Hydrochloride	174°	C <sub>17</sub> H <sub>18</sub> ClNO <sub>4</sub>	56.43	7.74	3.87	56.45	7.87	3.84
9	1,2,3,4-Tetrahydro- β-carboline	2	58.0	Free base	151°	C <sub>13</sub> H <sub>14</sub> N <sub>2</sub> O <sub>4</sub>	67.31	6.34	6.82	67.33	6.46	6.64
10	1,2,3,4-Tetrahydro- β-carboline	3	54.3	Hydrochloride Monohydrate	199°	C <sub>14</sub> H <sub>18</sub> ClN <sub>2</sub> O <sub>4</sub> ·H <sub>2</sub> O	60.19	6.48	5.85	59.99	6.52	5.75

<sup>a</sup>Reported (7) no yield melting point of the hydrochloride 199–200.5°.

<sup>b</sup>Reported (7) no yield melting point of the hydrochloride 156.5–157.5°.

<sup>c</sup>Reported (1, 7) low yield melting point of the hydrochloride 168°.





Lithium aluminum hydride reduction of V to IV had been attempted previously but without success (9). However, lithium aluminum hydride in boiling dioxane reduced V to IV in better than 90% yield. The reaction of IV with 2-chloroethyl 3,4,5-trimethoxybenzoate (I) and 3-chloropropyl 3,4,5-trimethoxybenzoate (II) was carried out in dimethylformamide solution using anhydrous potassium carbonate as the acid acceptor.

#### EXPERIMENTAL

Melting points are uncorrected. Microanalyses were carried out at the Microanalytical Laboratory of E. Thommen, Thannerstrasse 45, Basel, Switzerland.

##### 3,4,5-Trimethoxybenzoyl Chloride

The procedure of Lasslo and Jordan (10) was followed except that the crude product was further purified by distillation *in vacuo*, b.p. 110–112°/0.5 mm.

##### 2-Chloroethyl 3,4,5-Trimethoxybenzoate (I)

A mixture of 23.05 g of 3,4,5-trimethoxybenzoyl chloride, 8.05 g of 2-chloroethanol, and 10 g of anhydrous potassium carbonate in 200 ml of dry benzene was stirred and refluxed for 4 hours. At the end of the reaction period the evolution of carbon dioxide ceased. The inorganic salts were separated by filtration. The benzene was distilled from the filtrate under reduced pressure and the remaining liquid was distilled *in vacuo*. The fraction boiling at 155–158°/1 mm was collected and further purified by recrystallization from aqueous alcohol. A yield of 18.1 g (66.1%), m.p. 72°, was obtained. Anal. Calc. for  $C_{17}H_{15}ClO_5$ : C, 52.46; H, 5.46; Cl, 12.91. Found: C, 52.33; H, 5.40; Cl, 13.15.

##### 3-Chloropropyl 3,4,5-Trimethoxybenzoate (II)

The same procedure as in the case of 2-chloroethyl 3,4,5-trimethoxybenzoate was used. A yield of 68.3%, b.p. 162–164° (1 mm) and m.p. 58° (aqueous ethanol), was obtained. Anal. Calc. for  $C_{13}H_{17}ClO_5$ : C, 54.08; H, 5.89; Cl, 12.28. Found: C, 54.31; H, 6.01; Cl, 12.00.



*2-Piperidinoethyl 3,4,5-Trimethoxybenzoate*

2-Chloroethyl 3,4,5-trimethoxybenzoate (5.49 g, 0.02 mole) was dissolved in 20 ml of freshly distilled piperidine. The reaction mixture was refluxed for 3 hours while a semi-solid material separated. The mixture was cooled and then treated with 25% aqueous sodium hydroxide and extracted thoroughly three times with chloroform. The chloroform layer was washed with water and dried over sodium sulphate. Distillation of the chloroform and the excess of piperidine under reduced pressure left an oily residue which did not crystallize. It was dissolved in chloroform and a slow stream of dry hydrogen chloride was passed through the solution for 15 minutes. Addition of ether precipitated the hydrochloride which was recrystallized from a mixture of isoamyl alcohol and ethyl acetate; 5.2 g (72.3%) of 2-piperidinoethyl 3,4,5-trimethoxybenzoate hydrochloride was obtained melting at 209–210°. Anal. Calc. for  $C_{17}H_{26}ClNO_5$ : C, 56.75; H, 7.23; Cl, 9.86; N, 13.89. Found: C, 56.92; H, 7.48; Cl, 10.07; N, 4.07. The picrate, m.p. 165–166°, was recrystallized from alcohol. Anal. Calc. for  $C_{23}H_{28}N_4O_{12}$ : C, 50.00; H, 5.07; N, 10.14. Found: C, 49.91; H, 5.22; N, 10.51. The remaining compounds in the series were prepared as above, and are listed in Table I.

*Piperid-2,3-dione-3-phenylhydrazone*

Piperid-2,3-dione-3-phenylhydrazone was prepared from 3-carbethoxy-2-piperidone according to the procedure of Abramovitch and Shapiro (9).

*1,2,3,4-Tetrahydro-1-oxo- $\beta$ -carboline*

Fifty-eight grams of piperid-2,3-dione-3-phenylhydrazone (m.p. 244–245°) was added to a mixture of 135 ml of concentrated hydrochloric acid and 270 ml of glacial acetic acid. The reaction mixture was stirred and refluxed for 3 hours. The dark solution obtained was treated with charcoal and filtered. The filtrate was distilled under reduced pressure. The remaining dark material was treated with 75 ml of ice-cold acetone. The acetone was decanted and the residue was recrystallized from boiling acetone. The crystalline material obtained was recrystallized from aqueous alcohol and melted at 183–185°. Repeated crystallization from aqueous alcohol raised the melting point to 188°. Reported 183–184° (9), 189° (11). A yield of 26 g (49%) was obtained.

*1,2,3,4-Tetrahydro- $\beta$ -carboline*

A sample of 1,2,3,4-tetrahydro-1-oxo- $\beta$ -carboline (9.5 g) was dried *in vacuo* over phosphorous pentoxide and subsequently dissolved in 125 ml of boiling dry dioxane. This solution was added dropwise to a stirred and refluxing suspension of 9.5 g powdered lithium aluminum hydride in 200 ml of dioxane. During the addition the dioxane refluxed smoothly without external heating. The reaction mixture was stirred and refluxed in a nitrogen atmosphere for 4 hours and then was cooled. The excess of lithium aluminum hydride was destroyed with wet dioxane.

The mixture was brought to boiling and filtered hot. The dioxane was evaporated under reduced pressure and the solid residue was recrystallized from aqueous alcohol; 8.4 g (95.7%) of 1,2,3,4-tetrahydro- $\beta$ -carboline, m.p. 208° (reported 200–202° (9), 204° (12)), was obtained. It gave a picrate melting at 253° with decomposition (reported 253° dec. (9, 11)).

*2-(1,2,3,4-Tetrahydro- $\beta$ -carbolinyl-2)ethyl 3,4,5-Trimethoxybenzoate*

A mixture of 1.72 g (0.01 mole) of 1,2,3,4-tetrahydro- $\beta$ -carboline, 2.74 g (0.01 mole) of 2-chloroethyl 3,4,5-trimethoxybenzoate, and 4 g of anhydrous potassium carbonate in

10 ml of dimethylformamide was stirred and refluxed for 4 hours. The reaction mixture was cooled and then filtered. The inorganic salts remaining on the filter were washed with dimethylformamide. The combined filtrates were distilled under reduced pressure until all the dimethylformamide was removed. The residue was dissolved in 100 ml of chloroform and passed through an alumina column which was eluted with an additional 150 ml of chloroform. The chloroform was removed from the combined eluates by distillation and the residual oil crystallized on trituration with a few drops of methanol. It was recrystallized from methanol and melted at 151°. Yield of 2.38 g (58%) was obtained. Anal. Calc. for  $C_{23}H_{26}N_2O_5$ : C, 67.31; H, 6.34; N, 6.82. Found: C, 67.33; H, 6.46; N, 6.64.

*3-(1,2,3,4-Tetrahydro- $\beta$ -carbolinyl-2)propyl 3,4,5-Trimethoxybenzoate*

This compound was prepared as above, except that it was isolated as the hydrochloride hydrate. The eluate from the alumina column was treated with dry hydrogen chloride. Upon addition of ether an oil was deposited which crystallized on trituration. It was recrystallized from isoamyl alcohol to yield 2.6 g (54.3%), m.p. 199–200°. Anal. Calc. for  $C_{24}H_{29}ClN_2O_5 \cdot H_2O$ : C, 60.19; H, 6.48; N, 5.85. Found: C, 59.99; H, 6.52; N, 5.75.

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## HEATS OF MIXING OF POLYISOBUTYLENE WITH SOME ORGANIC SOLVENTS<sup>1</sup>

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### ABSTRACT

The heats of mixing of four fractions of polyisobutylene with five organic solvents have been measured at 25° C with the use of a Tian-Calvet microcalorimeter. The maximum concentrations attained were of the order of 3% in polymer. It has been found that the enthalpy parameter  $\kappa_0$  is independent of the molecular weight of the polymer sample in the investigated molecular weight range. All the values for  $\kappa_0$  calculated from the Van Laar - Scatchard equation for the different polymer-solvent pairs are different from the values estimated from the partial molal quantities. This is explained with the use of new theories on the thermodynamics of high polymer solutions by Orofino and Flory and by Huggins.

### INTRODUCTION

The physical state of a pure polymer at rest is ill-defined. For many types of high polymers, their state presents some degree of crystallinity or molecular orientation but most polymers are amorphous except under special conditions. Polyisobutylene is an amorphous polymer but below -70° C, its molecules are frozen in the so-called glassy state (1) and the transition from that state to the "liquid" state takes place over a rather wide temperature range. However, at room temperature, the dissolution of pure polyisobutylene in a liquid solvent will probably not involve any heat of transition. This investigation has been carried out to check that hypothesis and to show the importance of the data on heats of mixing for the study of high polymer solutions.

### EXPERIMENTAL PART

#### Materials

Four fractions of polyisobutylene have been used in this investigation. The fractions PD-5 ( $\bar{M}_v = 392,000$ ) and PD-6 ( $\bar{M}_v = 252,000$ ) have been obtained from a fractionation of commercial Vistanex L-100 having a viscosity average molecular weight of about 1,360,000. The fractions PIJ-1-2 ( $\bar{M}_v = 108,000$ ) and PIJ-4 ( $\bar{M}_v = 63,000$ ) have been obtained from a fractionation of commercial Vistanex MH having a viscosity average molecular weight of about 68,000. Both commercial polymer samples have been obtained through the courtesy of Enjay Co., Inc. The fractionations have been carried out in accordance with previous procedures (2) and the molecular weights determined by the usual viscosity treatment of cyclohexane solutions. The reagent-grade solvents were purified in a high efficiency distilling column and stored over sodium wire.

#### Apparatus

The calorimetric measurements of the heats of mixing have been carried out using a Tian-Calvet microcalorimeter, a differential isothermal type which has been described elsewhere (3, 4). In our installation, a photopen recorder follows the spot of light reflected from the galvanometer mirror. The apparatus is calibrated electrically, and the measurement of the area under the curve gives the heat developed during the course of the reaction. This microcalorimeter is sensitive to a heat effect of 0.001 calorie per hour and is especially designed to follow a reaction over a long period of time.

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Contribution from the Department of Chemistry, Université de Montréal, Montreal, Que. This paper has been presented in part at the Eighth Canadian High Polymer Forum at McDonald College, Ste Anne de Bellevue, Que., May 12-14, 1958.

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The dissolution of the polymer was realized in a very simple way (5). A given quantity of polymer was weighed in a stainless steel mesh cage which was attached to a stainless steel wire and immersed under a quantity of mercury in a stainless steel cell. A weighed amount of solvent was added and the cell tightly stoppered. After thermal equilibrium was attained, the cage was then raised into the solvent and the thermal phenomenon measured.

### RESULTS

The data obtained in this investigation are given in Table I. In this table,  $m$  is the weight of polymer used in each experiment;  $V_M$ , the total volume of the mixture;  $\phi$ , the volume fraction of the polymer; and  $\Delta H_M$ , the integral heat of mixing. The quantity  $B_0$  represents the characteristic interaction constant for a given polymer-solvent pair and is calculated from the Van Laar - Scatchard equation, supposing that there is no volume change upon mixing,

$$[1] \quad \Delta H_M = B_0 V_M \phi (1 - \phi).$$

### DISCUSSION

Within the experimental errors, the values of  $B_0$  for fractions PIJ-4 and PD-6 with chlorobenzene are practically the same. So, there is no significant variation of  $B_0$  with molecular weight, at least in the range we have investigated. A résumé of the data is given in Table II and one sees that there is a direct relation between the Flory temperature  $\theta$  and the enthalpy parameter  $\kappa_0$  as predicted by theory. The parameter  $\kappa_0$  is related to  $B_0$  by the following equation

$$[2] \quad \kappa_0 = B_0 V_1 / RT$$

where  $V_1$  is the molar volume of the solvent.

However, the calculated values for  $\kappa_0$  are all different from those given for  $\kappa_1$ . The parameter  $\kappa_1$  is calculated from the partial molal quantities obtained by direct measurement of the heat of dilution or by indirect methods as viscosimetry, osmometry, and vapor pressure measurements. The large differences between the two sets of values for the enthalpy parameters may be due to three factors: (a) there may be an important volume change upon mixing, (b) there may be an important transition in the polymer state upon mixing, and (c) there may be a real difference between  $\kappa_0$  and  $\kappa_1$ . The first factor is readily rejected since the volume changes are rather slight in the concentration range we have investigated. For example, the specific volume of pure polyisobutylene is 1.094 cc/g at 25° C (7); in dilute benzene solutions, the partial specific volume of the polymer increases to a constant value of 1.105 cc/g (8). The value of  $\kappa_0$  would be increased to 0.70 because of this volume change upon mixing and the discrepancy with  $\kappa_1$  would be still greater.

The possibility of the existence of a heat of transition will now be considered. If we assume that the difference between the values of the heats of dissolution of polyisobutylene in benzene as measured in this investigation and those calculated with  $\kappa_1 = 0.21$  is due to some heat of transition, we come to the conclusion that the value for this heat is approximately 185 calories per monomer unit, a value which is not too high when compared with those obtained for other polymers. But this value should be independent of the nature of the solvent, and in athermal or slightly exothermic solvents as cyclohexane and *n*-heptane (see Table II), this endothermic heat of transition should have shown up.

TABLE I  
Heats of mixing of polyisobutylene with some organic solvents at 25° C

<i>m</i> , g	<i>V</i> <sub>m</sub> , ml	φ	Δ <i>H</i> <sub>M</sub> , cal	<i>B</i> <sub>0</sub> , cal/ml
Fraction PIJ-4 in benzene				
0.046 <sub>0</sub>	7.052	0.00714	0.218	4.35
0.073 <sub>8</sub>	5.787	0.0139	0.352	4.44
0.082 <sub>2</sub>	5.311	0.0169	0.391	4.42
0.086 <sub>8</sub>	4.979	0.0191	0.413	4.44
0.080 <sub>7</sub>	3.836	0.0230	0.376	4.36
0.077 <sub>5</sub>	3.404	0.0249	0.360	4.35
0.088 <sub>6</sub>	3.477	0.0279	0.423	4.48
0.094 <sub>7</sub>	3.622	0.0286	0.438	4.35
0.126 <sub>0</sub>	3.973	0.0347	0.579	4.35
0.143 <sub>4</sub>	4.274	0.0367	0.657	4.35
0.090 <sub>3</sub>	2.618	0.0377	0.425	4.46
0.284 <sub>7</sub>	5.244	0.0593	1.304	4.45
Fraction PIJ-4 in chlorobenzene				
0.033 <sub>8</sub>	6.555	0.00559	0.101	2.77
0.050 <sub>4</sub>	6.035	0.00914	0.155	2.83
0.059 <sub>4</sub>	6.014	0.0108	0.184	2.86
0.066 <sub>2</sub>	6.008	0.0121	0.209	2.91
0.083 <sub>5</sub>	6.069	0.0151	0.255	2.83
0.089 <sub>2</sub>	6.079	0.0161	0.282	2.94
0.137 <sub>5</sub>	8.443	0.0178	0.433	2.93
0.122 <sub>3</sub>	6.144	0.0218	0.385	2.93
0.127 <sub>7</sub>	6.135	0.0226	0.380	2.81
0.155 <sub>4</sub>	6.121	0.0278	0.483	2.92
0.160 <sub>3</sub>	6.138	0.0286	0.508	3.00
0.215 <sub>8</sub>	6.217	0.0379	0.665	2.92
Fraction PD-6 in chlorobenzene				
0.023 <sub>8</sub>	6.137	0.00420	0.071	2.77
0.037 <sub>8</sub>	6.928	0.00594	0.122	2.99
0.039 <sub>0</sub>	6.350	0.00671	0.125	2.95
0.041 <sub>0</sub>	5.983	0.00749	0.125	2.81
0.047 <sub>9</sub>	6.033	0.00869	0.150	2.86
0.051 <sub>9</sub>	6.192	0.00917	0.161	2.86
0.066 <sub>2</sub>	6.286	0.0115	0.218	3.03
0.076 <sub>8</sub>	6.133	0.0137	0.239	2.89
0.083 <sub>1</sub>	6.071	0.0152	0.266	2.93
0.085 <sub>4</sub>	6.023	0.0155	0.267	2.90
0.118 <sub>8</sub>	6.191	0.0210	0.384	3.02
0.116 <sub>3</sub>	6.068	0.0210	0.381	3.14
Fraction PD-6 in ethylbenzene				
0.038 <sub>2</sub>	6.072	0.00688	0.082	1.98
0.046 <sub>8</sub>	6.231	0.00807	0.097	1.93
0.060 <sub>9</sub>	6.489	0.0103	0.126	1.91
0.070 <sub>8</sub>	6.338	0.0121	0.152	2.00
0.083 <sub>3</sub>	6.423	0.0142	0.174	1.94
0.084 <sub>1</sub>	6.316	0.0146	0.173	1.91
0.085 <sub>8</sub>	6.378	0.0147	0.176	1.90
0.089 <sub>8</sub>	6.304	0.0156	0.200	2.06
0.100 <sub>8</sub>	6.244	0.0177	0.211	1.95
0.101 <sub>7</sub>	6.172	0.0180	0.206	1.88
0.121 <sub>1</sub>	6.407	0.0207	0.259	2.00
0.189 <sub>8</sub>	6.289	0.0330	0.363	1.81
Fraction PIJ-4 in cyclohexane				
0.194 <sub>8</sub>	6.642	0.0321	-0.027	-0.13
0.194 <sub>0</sub>	6.551	0.0324	-0.043	-0.21
Fraction PD-6 in <i>n</i> -heptane				
0.059 <sub>7</sub>	6.266	0.0104	-0.029	-0.45
0.085 <sub>3</sub>	6.138	0.0152	-0.037	-0.40
0.243 <sub>2</sub>	6.240	0.0426	-0.097	-0.38

TABLE II  
Résumé of data on heat parameters for polyisobutylene in some  
organic solvents at 25° C

Solvent	$\theta$ , °K	$\kappa_0$	$\kappa_1$
Benzene	297.7 <sup>a</sup>	0.66	0.21 (cal.) <sup>c</sup>
Chlorobenzene	262 <sup>b</sup>	0.50	0.15 (vis.) <sup>b</sup>
Ethylbenzene	251 <sup>a</sup>	0.40	0.117 (vis.) <sup>a</sup>
Cyclohexane	126 <sup>a</sup>	-0.03	0.059 (vis.) <sup>a</sup>
			0.07 (osm.) <sup>d</sup>
<i>n</i> -Heptane	0 <sup>a</sup>	-0.10	0 (vis.) <sup>a</sup>

NOTE: cal.: calorimetry; vis.: viscosimetry; osm.: osmometry.

<sup>a</sup>See reference 1.

<sup>b</sup>M. Senez, M.Sc. Thesis, Université de Montréal, Montreal, Que., 1958.

<sup>c</sup>See reference 6.

<sup>d</sup>P. J. Flory and H. Daoust, J. Polymer Sci. **25**, 429 (1957).

Although we do not discard the possibility of the existence of some heat of transition, we believe that the data can be discussed in regard to a new approach to the theory of the heat of mixing. Recently, Orofino and Flory (9) and Huggins (10, 11) have published new theories on the thermodynamics of high polymer solutions. The new semiempirical equation proposed by Orofino and Flory for the free energy of mixing is given by

$$[3] \quad \Delta F_M = RT\{n_1 \ln(1-\phi) + n_2 \ln \phi + xn_2[\chi_0 - \sum_{i=1} (\chi_i/i)\phi^i]\}$$

where  $n_1$  and  $n_2$  are the number of moles of the solvent and the polymer in the mixture and  $x$  is the ratio of the molar volumes of the polymer and the solvent,  $V_2/V_1$ . This equation has been derived to account for the polymer-solvent pairs for which a single interaction parameter cannot be used. The physical meaning of the parameters  $\chi_0$ ,  $\chi_1$ , is not given but each of them is assumed to be independent of the concentration of the solution. From the equation [3], through the use of standard thermodynamic equations, the heat of mixing may be shown to be given by

$$[4] \quad \Delta H_M = -T^2[\partial(\Delta F_M/T)/\partial T]_p = RT\kappa_0 n_2 x - RT\kappa_1 n_2 x \phi - RT\kappa_2 n_2 x \phi^2 - \dots$$

where  $\kappa_1 = -T(\partial\chi_1/\partial T) = B_1 V_1/RT$ . Equation [4] may be reduced to equation [1] when  $\kappa_0 = \kappa_1$  and  $\kappa_2$  and higher parameters vanish.

The new equation proposed by Huggins for the heat of mixing of "liquid" polymers with liquid solvents is given by

$$[5] \quad \Delta H_M = N\Delta H_2^* n_2 - aN\Delta H_2^* n_2 \phi - bN\Delta H_2^* n_2 \phi^2 - \dots$$

where  $N$  is the Avogadro number and  $a$ ,  $b$ , etc. are fractional quantities. The quantity  $\Delta H_2^*$  is defined by Huggins as the increase of heat content when a single molecule of polymer is transferred from pure polymer to pure solvent. The sign and the magnitude of  $\Delta H_2^*$  are functions of the molecular structure of polymer and solvent and of the intermolecular forces involved in 1-1, 2-2, and 1-2 contacts.

The partial molal quantities derived from equations [3], [4], or [5] will not contain any interaction parameter with the subzero index and the results obtained from measurements of the integral heat of mixing and the results obtained from measurements of the heat of dilution may give different values for the heat parameter at infinite dilution. Even if there is a real difference between  $\kappa_0$  and  $\kappa_1$  as predicted by Huggins' treatment, this



difference should not be very large for mixtures of monomers since the molecular configuration changes are minor in that case. But in the case of a mixture of a polymeric solute in a monomeric solvent,  $RT\kappa_0 n_2 x$  or  $\Delta H_2^* N n_2$ , which represents the energy change when  $N n_2$  macromolecules are transferred from their pure state to their solute state, depends on the degree of self-coiling of the chains which in turn depends on the polymer-solvent specific interactions. The sudden change in the configuration of the polymer chains upon mixing in a poor solvent will then be responsible for the large difference between the mixing parameter  $\kappa_0$  and the infinite dilution parameter,  $\kappa_1$ .

The process of mixing may be considered as a series of dilutions starting with  $\phi = 1$  and according to the results shown in Table II, the dilution of a very concentrated polymer solution would produce a higher apparent heat parameter than the dilution of a less concentrated solution. This observation has been confirmed by calorimetric measurements (6) and indirect measurements (12) of the heats of dilution of the polyisobutylene-benzene system for which the apparent heat parameter increases from 0.21 at high dilution to approximately 0.6 at very high polymer concentration. The major part of the enthalpy of mixing for that system would thus come from the first neighbor interaction between polymer and solvent molecules and from the molecular configuration changes of the polymeric chains due to this interaction at the beginning of the mixing process.

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# THE INFRARED FREQUENCIES AND INTENSITIES OF THE HYDROXYL GROUP IN 2,6-DI-*tert*-BUTYL-4-SUBSTITUTED PHENOLS<sup>1</sup>

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## ABSTRACT

The infrared frequencies, intensities, and apparent half band widths of the O—H stretching band of a series of 2,6-di-*tert*-butyl-4-substituted phenols have been measured in carbon tetrachloride solution and compared with the corresponding 4-substituted phenols. The frequencies of the former are 36 cm<sup>-1</sup> higher than the latter and the intensities are also slightly higher. Both the frequency and intensity follow a Hammett  $\rho\sigma$  relation. It is shown that the O—H bond lies in the plane of the benzene ring, the increase in frequency and intensity being ascribed to a steric repulsion of the phenolic hydrogen by the adjacent *tert*-butyl group.

## INTRODUCTION

Previous work on the frequencies and intensities of the hydroxyl group of substituted phenols has dealt mainly with meta- and para-monosubstitution (1, 2, 3, 4), although some work has been done on the effects of orthosubstituents (5) and the frequencies of a few 2,6-di-*tert*-butyl phenols have been measured, but not with high precision (6, 7).

The present work was devoted mainly to the changes in frequency, intensity, and half band width produced by various 4-substituents on the O—H band in 2,6-di-*tert*-butyl phenols. The corresponding monosubstituted phenols were also examined.

## EXPERIMENTAL

A Beckman I.R.4 spectrophotometer with lithium fluoride optics was used to measure the O—H bands, the frequencies being calibrated by the standard absorption lines of water vapor. The effective slit width was about 4 cm<sup>-1</sup>. Band areas were obtained by graphical integration. Solution concentrations in the range 0.01–0.005 molar were employed and the cell thickness was 1.0 mm. At this concentration even the sterically non-hindered phenols show no evidence of hydrogen bonding in carbon tetrachloride.

The preparation of most of the compounds employed has been described previously (8)\* but the preparation of 2,6-di-*tert*-butyl-4-methoxyphenol deserves some discussion as the present data in the literature are somewhat misleading. First attempts to prepare this compound by the butylation of *p*-methoxyphenol in petroleum ether with isobutylene and sulphuric acid at 50° C (9) gave, after recrystallization from *n*-hexane, a 60% yield of a product, m.p. 103.5–104.5° C. Analysis: Found: C, 76.5; H, 10.1; CH<sub>3</sub>O, 13.4. Calculated for C<sub>15</sub>H<sub>24</sub>O<sub>2</sub>: C, 76.22; H, 10.24; CH<sub>3</sub>O, 13.13. The melting point agrees with a previously reported value (6), but both the frequency and intensity of the O—H band were much lower than expected. The required phenol has also been reported by Müller and Ley (7), who prepared it from 4-methoxy-2,4,6-tri-*tert*-butyl-2,5-cyclohexadiene-1-one. Their product melted at 106–107° and they also obtained an identical compound by the butylation of *p*-methoxyphenol in 84% yield, but with recrystallization from methanol.

An examination of the spectrum of the raw product obtained by butylating *p*-methoxyphenol showed two bands, the larger corresponding to the product already separated (m.p. 103.5–104.5) and the smaller having the frequency expected for 2,6-di-*tert*-butyl-

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\*References to the original preparations are given in reference 8.

4-methoxyphenol. The two components were readily separated by an initial recrystallization from *n*-hexane to remove a large amount of the compound previously obtained, followed by recrystallization twice from methyl alcohol to yield the second component, m.p. 106–107° C. Analysis: Found: C, 76.2; H, 10.1; CH<sub>3</sub>O, 15.0.

The lower melting compound must be 2,5-di-*tert*-butyl-4-methoxy phenol and the higher the 2,6-compound. The structural assignments were made on the basis of O—H frequency (see Discussion) since the 1600–2000 cm<sup>-1</sup> region is too complicated to give unequivocal results. The assignments were confirmed by gas phase chromatography through a polar column (polyester succinate), the 2,6-compound having a retention time of about one third of the 2,5-compound, which is in agreement with similar hindered and non-hindered phenols. Adsorption chromatography on alumina of the raw butylated product showed that the ratio of 2,6 to 2,5 is 3:7. The high yield previously reported (7) must be because the reported yields are based on raw product, not on the purified material.

### RESULTS

The frequency of the band maximum  $\nu_m$ , intensity  $A$ , and apparent half band widths  $\Delta\nu_{1/2}^a$  for the phenols examined are given in Table I. The intensities have been corrected for wing absorption (10) and are given in units of  $1 \times 10^4$  mole<sup>-1</sup> liter cm<sup>-2</sup> using  $\log_{10}(I_0/I)$ . The frequencies are probably correct to within about 1 cm<sup>-1</sup>. The results obtained with monosubstituted phenols in carbon tetrachloride are in good agreement with previous work. The solvent 1,2-dichloroethane was used in order to get the hydroxy and nitro derivatives of phenol into solution in 0.01 molar concentration for intensity measurements. Since this solvent had such a pronounced effect on the O—H band, the other monosubstituted phenols were also examined in this solvent for comparative purposes.

TABLE I

Frequencies, intensities, and apparent half band widths of the O—H stretching band in substituted phenols

Substituent	$\Sigma\sigma$ (12)	$\nu_m(\text{cm}^{-1})$			$1 \times 10^4 A \text{ mole}^{-1}$ liter cm <sup>-2</sup>			$\Delta\nu_{1/2}^a(\text{cm}^{-1})$		
		<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
4-NO <sub>2</sub>	1.270	3592	3538	3626. <sub>s</sub>	0.82	1.49	0.84	25	71	15. <sub>s</sub>
4-CHO	1.126	3595. <sub>s</sub>	3541. <sub>s</sub>	3630	0.83	1.49	0.80	24. <sub>s</sub>	67	16
4-CN	1.000	3595. <sub>s</sub>		3631	0.75		0.79	24		14. <sub>s</sub>
3-NO <sub>2</sub>	0.710	3600	3549		0.70	1.30		22	64	
3-Cl	0.373	3604	3557. <sub>s</sub>		0.63	1.14		21	62	
4-Cl	0.227	3607. <sub>s</sub>	3561	3643. <sub>s</sub>	0.62	1.12	0.60	20	59	15
—	0.000	3609. <sub>s</sub>	3566	3645. <sub>s</sub>	0.55	1.04	0.57	18	53	16. <sub>s</sub>
4-(CH <sub>3</sub> ) <sub>2</sub> NCH <sub>3</sub>				3646			0.62			17
3-CH <sub>3</sub>	-0.069	3610			0.55			18. <sub>s</sub>		
4-C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> C		3610. <sub>s</sub>		3647	0.58		0.58	17. <sub>s</sub>		18
4-C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )CH	-0.123	3612. <sub>s</sub>		3648	0.53		0.54	16		17
4-CH <sub>3</sub>	-0.170	3612	3569. <sub>s</sub>	3648	0.50	0.98	0.53	16	51	18. <sub>s</sub>
4-C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> ) <sub>2</sub> C	-0.190	3612		3647	0.57		0.53	16. <sub>s</sub>		18
4-(CH <sub>3</sub> ) <sub>2</sub> C	-0.197	3611	3569	3647. <sub>s</sub>	0.51	0.98	0.55	16. <sub>s</sub>	48	18. <sub>s</sub>
4-CH <sub>3</sub> O	-0.268	3615	3574	3649	0.50	0.95	0.51	17. <sub>s</sub>	50	20. <sub>s</sub>
4-OH	-0.357	3614. <sub>s</sub>	3574. <sub>s</sub>	3649		0.96	0.49	15. <sub>s</sub>	49	20
4-CH <sub>3</sub> O-3-C(CH <sub>3</sub> ) <sub>3</sub>	-0.388	3615			0.50			18		
4-OH-3,5-di-C(CH <sub>3</sub> ) <sub>3</sub>	-0.597	3615			0.51			18		
4-NH <sub>2</sub>	-0.660	3616	3576	3650. <sub>s</sub>			0.45	15	46	22

NOTE: (a) Phenols in CCl<sub>4</sub>; (b) phenols in (CH<sub>2</sub>Cl)<sub>2</sub>; (c) 2,6-di-*tert*-butyl phenols.

The results given in Table I can be correlated by a Hammett  $\rho\sigma$  relation (1-5) as is shown in Figs. 1, 2, and 3. In Fig. 2 the intensities relative to phenol and to 2,6-di-*tert*-

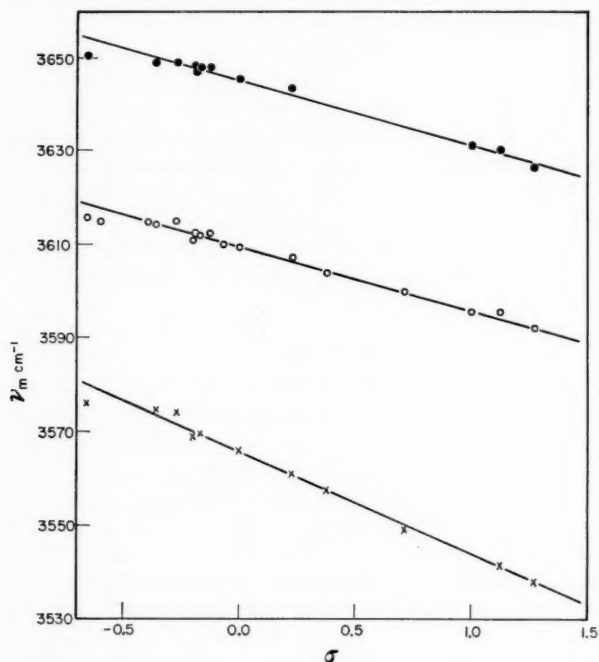


FIG. 1. Wavelength of O—H band against  $\sigma$ .  $\circ$  = Phenols in  $\text{CCl}_4$ ;  $\times$  = phenols in  $(\text{CH}_2\text{Cl})_2$ ;  $\bullet$  = 2,6-di-*tert*-butyl phenols in  $\text{CCl}_4$ .

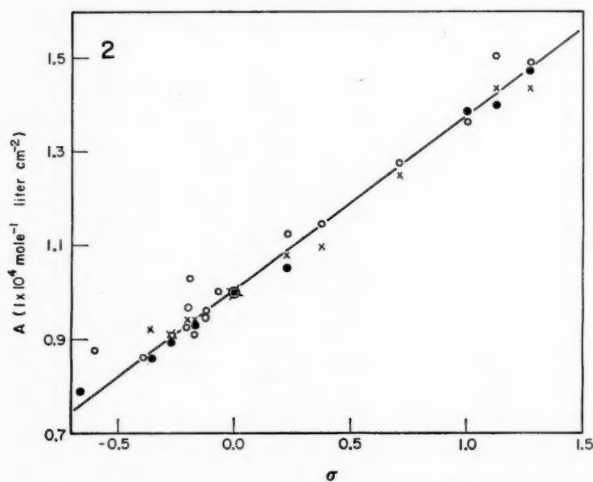


FIG. 2. Intensity of O—H band against  $\sigma$ .  $\circ$  = Phenols in  $\text{CCl}_4$ ;  $\times$  = phenols in  $(\text{CH}_2\text{Cl})_2$ ;  $\bullet$  = 2,6-di-*tert*-butyl phenols in  $\text{CCl}_4$ .

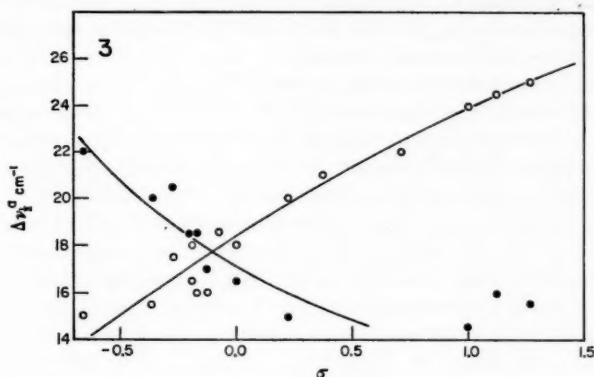


FIG. 3. Apparent half band width of O—H band against  $\sigma$ . ○ = Phenols in  $\text{CCl}_4$ ; ● = 2,6-di-*tert*-butyl phenols in  $\text{CCl}_4$ .

butyl phenol have been plotted against  $\sigma$ . It is obvious that a good straight line can be obtained without the necessity of plotting  $\log A$  against  $\sigma$  (4, 11). With regards to the determination of band intensities, Ramsay (10) has suggested a simple formula for computing the true intensity in terms of the observed peak absorbance and apparent half band width. Values calculated by means of this formula were found to be higher than the directly measured intensities by between 10 and 20% (4).

#### DISCUSSION

The increase in frequency observed with the 2,6-di-*tert*-butyl-4-substituted phenols compared with the corresponding unhindered phenols is too large ( $36\text{ cm}^{-1}$ ) to be accounted for by the resonance and inductive contribution of the two *tert*-butyl groups.  $\sigma$  Values for orthosubstituents have recently been derived by Taft (13) and are generally close to the  $\sigma_{\text{para}}$  values for the same substituent. At first sight the increase might therefore be attributed to the twisting of the O—H bond out of the plane of the benzene ring which would decrease the resonance interaction and increase the bond order and therefore the frequency. However, it can be seen from Fig. 1 that the lines through the phenols and the 2,6-di-*tert*-butyl phenols in  $\text{CCl}_4$  are parallel. Both types of phenols must, therefore, have a similar structure since, if the O—H bond were twisted out of the plane of the ring, resonance interaction between the O—H and the strongly electron-attracting groups would be decreased. For example,  $\sigma$  para- $\text{NO}_2$  has a value of 1.27 for phenols (and for anilines) but for other compounds its  $\sigma_{\text{para}}$  value is 0.78. If the O—H bond were at right angles to the benzene plane, the latter  $\sigma$  value for  $\text{NO}_2$  should be observed and, if it lies between 0 and  $90^\circ$ , an intermediate value. It must, therefore, be concluded that the O—H bond is in the plane, further verification being the use of the larger  $\sigma_{\text{para}}$  values (to be used with phenols and anilines) for the CN and CHO group.

This conclusion has been verified by examining the characteristic group frequencies of certain of the *p*-substituents. The results are given in Table II. It has been shown that the frequencies of all these groups follow a Hammett  $\rho\sigma$  plot (5, 14, 15, 16). Therefore, if the OH bond is twisted out of the plane by the *tert*-butyl groups, the effective  $\sigma$  will be less than the sum of the  $\sigma$  for O—H para ( $-0.36$ ) plus two *tert*-butyl groups (meta) ( $2 \times -0.12$ ), i.e. less than  $-0.60$  (17) and, therefore, the frequency shifts ( $\Delta\nu_m$ ) given in

Table II will not be in the ratio 3:5; but, if the OH bond is in the plane, the frequency shifts will be in proportion to  $\Sigma\sigma$ , i.e. 3:5. If the O—H is tilted up from plane, the angle can be calculated from the measured ratio of the frequency shifts (17). It is apparent that with the strongly electron-attracting groups CHO and CN in the para position the O—H bond lies in the plane. The results for the OH and NH<sub>2</sub> group are more ambiguous. It seems improbable that the structure changes as drastically as the results might suggest (i.e. angle to the plane  $\sim 35^\circ$  in OH case). It seems more probable that we are dealing here with a saturation of the electronic effects produced by the four electron-releasing groups on the ring because, if the hindered O—H was tilted to the plane, its frequency would be expected to increase whereas with the parasubstituents NH<sub>2</sub> and OH the frequency is slightly below the expected value. This saturation effect is also observed with the ordinary phenols (where there is no steric force tending to push the O—H out of the plane) when  $\sigma > -0.4$ .

TABLE II  
Influence of a hindered hydroxyl group on the bond properties of parasubstituents

Compound	$\Sigma\sigma$ (12)	X = CHO		X = CN		X = OH		X = NH <sub>2</sub>					
		$\nu_m$ $\Delta\nu_m$		$\nu_m$ $\Delta\nu_m$		$\nu_m$ $\Delta\nu_m$		Antisymmetric		Symmetric		$A_{anti}$	
		$\nu_m$	$\Delta\nu_m$	$\nu_m$	$\Delta\nu_m$	$\nu_m$	$\Delta\nu_m$	$\nu_m$	$\Delta\nu_m$	$\nu_m$	$\Delta\nu_m$	$A_{sym}$	
C <sub>6</sub> H <sub>5</sub> X	0.00	1710	0	2230.5	0	3609.5	0	3481	0	3396	0	0.93	
4HOC <sub>6</sub> H <sub>4</sub> X	-0.36	1701	-9	2228.4	-1.5	3614.4	5	3456	25	3380	16	3.0	
3,5-di-C(CH <sub>3</sub> ) <sub>2</sub> -4HOC <sub>6</sub> H <sub>3</sub> X	-0.60	1695	-15	2227.3	-2.5	3615.0	5.5	3455	26	3379	17	1.5	

Absolute intensities of the bands of the groups in Table II were not measured (with the exception of (OH)), but the ratio of the intensities of the two N—H bands was measured. The ratio for aniline is in fair agreement with the value reported previously (16) and for 2,6-di-*tert*-butyl-4-amino phenol is within the expected range for  $\Sigma\sigma = -0.60$ ; the large ratio for *p*-hydroxy aniline is quite unexpected. It is also surprising that the half band width of the CN group of 2,6-di-*tert*-butyl-4-cyano phenol is twice as great as for the other two cyano compounds (15).

A stereochemical configuration with the hindered O—H in the benzene plane can be seen to be quite plausible by the use of molecular models and we have checked this by calculating the position of the phenolic hydrogen relative to the adjacent *tert*-butyl group placed in the most favorable configuration. Using Pauling's (18) values for the van der Waal's radii of the atoms, the interpenetration of the phenolic hydrogen with each of four equivalent hydrogens is 0.25 Å and is about the same with the two equivalent carbons. This suggests a total compression energy of the order of 0.1–0.2 kcal/mole (19), which is very much smaller than the resonance energy gained by keeping the O—H bond in the plane ( $\sim 7.0$  kcal/mole (18)). Furthermore, these "rigid model" compressions are a maximum, a little flexibility in the bonds would reduce the compression energy even further.

The increase in frequency of the 2,6-di-*tert*-butyl phenols, over and above that due to the electropositivity of the two *tert*-butyl groups, must be due to the snug fitting of the phenolic hydrogen into the adjacent *tert*-butyl group. The repulsion of the latter will build up as the O—H bond stretches and will therefore narrow the potential energy curve, increase its asymmetry, and thereby raise the frequency and intensity. That is, since the repulsion is due to interpenetration of the electron clouds it is exerted primarily



on the electrons of the phenolic hydrogen, and only through them on the proton itself. Thus, the interpenetration process will tend to keep back the electrons more than the proton. This will increase the dipole moment of the bond ( $\mu$ ) and the more the O—H bond stretches the more the dipole moment will be increased; and so  $\partial\mu/\partial r$  will be increased and hence the intensity. This can be seen in Table I where, instead of the expected decrease in intensity (owing to the electropositivity of the two *tert*-butyl groups) of  $0.05 \times 10^4$  mole<sup>-1</sup> liter cm<sup>-2</sup> on going from phenol to 2,6-di-*tert*-butyl phenol, an increase of  $0.02 \times 10^4$  is instead observed. The similarity in the relative intensities of the two sets of phenols shown in Fig. 2 is to be expected if they have similar configurations.

The results given in Table III are arranged to show the effect of a single alkyl substituent ortho to the hydroxyl group. The  $\sigma$  constants given in the second column are derived from Jaffe (12) and Taft ortho factors (13) with certain exceptions. The  $\sigma$  values derived for ortho-*tert*-butyl and ortho-*tert*-amyl were obtained from  $\nu_m$  but it should be pointed out that these values probably only apply to this system. The  $\sigma$  values for the three multiple substituted phenols are derived from the ortho-*tert*-butyl value and regular  $\sigma$  values. They can be used to calculate the expected frequencies. For instance, the calculated value for 2,5-di-*tert*-butyl-4-methoxyphenol is 3611.3 cm<sup>-1</sup>, thus confirming the structure assigned to this compound. The predicted frequency for the corresponding 4-hydroxy phenol is 3612.5 cm<sup>-1</sup>. 2-*tert*-Butyl-4-hydroxyphenol should have two bands at 3610.9 and 3616.4; these are not resolved but the measured value of  $\nu_m$  is in close agreement with their average.

TABLE III  
Influence of a single orthosubstituent on phenols in CCl<sub>4</sub>

Substituent	$\Sigma\sigma$ (12)	$\nu_m$ , cm <sup>-1</sup>	$1 \times 10^4 A$ mole <sup>-1</sup> liter cm <sup>-2</sup>	$\Delta\nu_{\text{H}}$ , cm <sup>-1</sup>
—	0.000	3609. <sub>s</sub>	0.55	18
2-CH <sub>3</sub>	-0.17 (13)	3612	0.54	19
2-C <sub>2</sub> H <sub>5</sub>	-0.151	3611	0.49	18. <sub>s</sub>
2- <i>n</i> -C <sub>3</sub> H <sub>7</sub>	-0.126	3611	0.53	18
2-C(CH <sub>3</sub> ) <sub>3</sub>	0.26*	3606	0.47	16. <sub>s</sub>
2-iso-C <sub>4</sub> H <sub>9</sub>	-0.225	3612	0.46	16
2- <i>tert</i> -C <sub>4</sub> H <sub>9</sub>	0.15*	3607. <sub>s</sub>	0.53	19. <sub>s</sub>
4-CH <sub>3</sub> O-2,5-di-C(CH <sub>3</sub> ) <sub>3</sub>	-0.128	3610. <sub>s</sub>	0.42	16
4-OH-2,5-di-C(CH <sub>3</sub> ) <sub>3</sub>	-0.217	3610. <sub>s</sub>		14
4-OH-2-C(CH <sub>3</sub> ) <sub>3</sub>	-0.477 and -0.097	3612. <sub>s</sub>	0.46	18

\*See text.

The quite large positive value of  $\sigma$  for the *o*-*t*-butyl group in this system is rather surprising. A possible explanation is that the *tert*-butyl group effectively raises the barrier to rotation of the O—H group around the phenyl-oxygen bond. It can be seen with molecular models that interaction between the two groups can occur when the O—H bond is at right angles to the benzene plane. Although there is certainly a minimum in the potential energy curve when the O—H bond points directly toward the *tert*-butyl group, it is presumably not as deep as when it points away from it. This increased barrier to rotation means that the O—H is held more rigidly in the plane of the ring; increased resonance with the ring therefore occurs and the frequency drops. The results with the two ortho-amyl phenols confirms that this frequency decrease is caused by steric factors.

The solvent 1,2-dichloroethane was used for those phenols which were only very slightly soluble in carbon tetrachloride before it was realized that very thick cells ( $\sim 5$  cm)

could be used with the latter solvent. It can be seen from Fig. 1 that the frequency is decreased and that the difference increases as the substituents become more electron-attracting. This kind of an effect can readily be explained as being due to hydrogen bonding involving the structure  $\phi\text{—O—H} \dots (\text{CH}_2\text{Cl})_2$ . Such interaction will obviously increase as the acidity of the phenol increases. Effects of this nature may help to explain the failure of the Bauer and Magat equation to interpret frequency shifts in different solvents (20). In this connection it is interesting to note that although the intensities in dichloroethane are roughly twice as great as in carbon tetrachloride, the relative intensities in the two solvents are unaffected by the nature of the parasubstituent (15) (see Fig. 2).

The results given in Fig. 3 (in which the apparent half band widths are plotted against  $\sigma$ ) show one of the most striking differences between the hindered and unhindered phenols. No complete explanation can be advanced to account for the differences in the sign of the slopes of the lines. The values for the hindered phenols with strongly electronegative groups are undoubtedly somewhat larger than their true values owing to the effect of finite slit width (10). In the hindered phenols the O—H group cannot be solvated at the hydrogen end but only at the oxygen, and this must reduce the influence of the solvent on the band. The generally lower values of  $\Delta\nu_{\frac{1}{2}}$  for the hindered phenols compared with the unhindered may also be partly due to the effect of the *tert*-butyl groups in increasing the moments of inertia of the molecule. It is interesting to note that in all previous cases where frequencies and half band widths of benzene derivatives have been shown to obey a Hammett  $\rho\sigma$  relation, the slopes of these two functions have opposite sign (20) whereas with hindered phenols they have the same sign.

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# ALIPHATIC CHEMISTRY OF FLUORENE

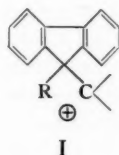
## PART V. SPIRO-KETONES<sup>1</sup>

P. M. G. BAVIN<sup>2</sup>

### ABSTRACT

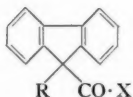
A novel synthesis is described of 1,2;3,4-dibenzophenanthrene, based on the spiro-ketone (IIIb), which was cleaved by strong base to the acid (VIIb).  
An example is described of acylation of aliphatic carbon.

The ease with which methyl fluorene-9-carboxylate anion reacts with a wide range of alkyl halides (1, 2, 3) together with the formation of phenanthrene derivatives from carbonium ions (I) prompted the investigations described in this paper.



It has been reported (4) that 9-benzylfluorene-9-carboxylic acid chloride (IIa) was cyclized by aluminum chloride to the spiro-ketone (IIIa), which may be converted via the alcohol (IVa) to 1,2;3,4-dibenzofluorene. This synthesis has been repeated and some yields improved. In particular, phosphorus pentoxide under boiling xylene rather than fused zinc chloride is the reagent of choice for dehydrating the alcohol (IVa).

The synthesis has been extended by the preparation and cyclization of 9-(2'-phenyl-ethyl)-fluorene-9-carboxylic acid (IIc), cyclization being effected by hydrogen fluoride. The homologous acid (IId) was unaffected by this reagent, in accord with the known

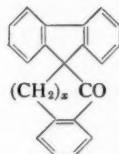


IIa, R = C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub>; X = Cl

IIb, R = C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub>; X = OH

IIc, R = C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub>CH<sub>2</sub>; X = OH

IId, R = C<sub>6</sub>H<sub>5</sub>·CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>; X = OH



IIIa, x = 1

IIIb, x = 2

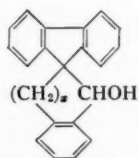
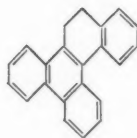
(5, p. 116) easier formation of six-membered ketones. All attempts to cyclize 9-(3'-phenylpropyl)-fluorene-9-carboxylic acid (IId) or its chloride have failed.

The formation of cyclic ketones from the tertiary acids is surprising since Lewis acids would have been expected to bring about decarbonylation. This exceptional behavior may be attributed to instability of the fluorene cation, which would be formed in the decarbonylation process (6).

<sup>1</sup>Manuscript received March 8, 1960.

Contribution from the Chemistry Department, the University, Hull, East Yorkshire, England.

<sup>2</sup>I.C.I. Fellow.

IVa,  $x = 1$ IVb,  $x = 2$ 

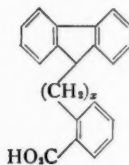
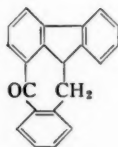
V

The ketone (IIIb) was converted via the alcohol (IVb) to 1,2,3,4-dibenzo-9,10-dihydro-phenanthrene (V). In agreement with earlier workers (7) the hydrocarbon could not be obtained crystalline but was dehydrogenated in good yield to 1,2,3,4-dibenzophenanthrene, completing a novel synthesis of this ring system. It was intended that this work should be extended to more complex ring systems, but lack of time has curtailed the work. Some 9-alkyl derivatives of methyl fluorene-9-carboxylate, prepared as desirable starting compounds, are described in the Experimental section. In addition, methyl 9-(4'-cyanobutyl)-fluorene-9-carboxylate has been prepared, as a possible precursor of VI. During its preparation, dimethyl butane-1,4-di-9'-fluorenyldi-9'-carboxylate was isolated as a by-product and identified by synthesis.

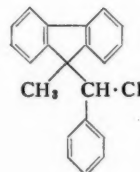


VI

The spiro-ketones (IIIa and IIIb) were cleaved by strong base, as expected for non-enolizable ketones, giving the acids (VIIa and VIIb), isomeric with (IIa and IIc). The direction of cleavage is controlled by formation of the more stable anion, as previously noted for 9-methyl-9-benzoylfluorene (8).

VIIa,  $x = 1$ VIIb,  $x = 2$ 

VIII



IX

The chloride of the acid (VIIa) reacted with aluminum chloride to reform the spiro-ketone (IIIa) and not, as had been hoped, the isomeric ketone (VIII). A few similar examples of acylation of aliphatic carbon are known, e.g. the acetylation and benzoylation of 9,10-dihydroanthracene (9).

The chloride prepared from the alcohol (IVa) closely resembled IX (8), decomposing at its melting point or in boiling formic acid with formation of 1,2,3,4-dibenzofluorene. Silver acetate in acetic acid gave unrearranged acetate. A similar stabilization of neopentyl-type carbonium ions by phenyl has been reported (10, and references quoted therein).

Other examples of non-rearrangement of neopentyl carbonium ions probably involve neighboring group participation (11). In agreement with this, the reaction between 9-methyl-9-fluorenylmethyl chloride and silver acetate gave 9-methylphenanthrene.

#### EXPERIMENTAL

Methyl fluorene-9-carboxylate anion was alkylated in the usual way (2) to give the following:

*9-Benzylfluorene-9-carboxylic acid*, prepared by saponification of the methyl ester (2), formed well-defined prisms from benzene-hexane, m.p. 204–205° (4). Found: C, 84.25; H, 5.24%. Calc. for  $C_{21}H_{16}O_2$ : C, 83.97; H, 5.37%.

*Methyl 9-(2'-phenylethyl)-fluorene-9-carboxylate* crystallized as long white needles (74%) from methanol, m.p. 67–68°. Found: C, 83.81; H, 5.99%. Calc. for  $C_{22}H_{20}O_2$ : C, 84.12; H, 6.14%. The *acid* (81%) crystallized as colorless rhombic plates from benzene-hexane, m.p. 143–144°. Found: C, 83.76; H, 5.66%. Calc. for  $C_{22}H_{18}O_2$ : C, 84.05; H, 5.77%.

*9-(3'-Phenylpropyl)-fluorene-9-carboxylic acid*, obtained by saponifying the oily methyl ester, formed large pale yellow prisms (76%) from benzene-hexane, m.p. 125–127°. Found: C, 84.11; H, 6.13%. Calc. for  $C_{23}H_{20}O_2$ : C, 84.12; H, 6.14%.

*Methyl 9-(2'-thienylmethyl)-fluorene-9-carboxylate* crystallized as small white needles (71%) from hexane, m.p. 104–105°. Found: C, 75.13; H, 5.17%. Calc. for  $C_{20}H_{16}O_2S$ : C, 74.99; H, 5.03%.

*Methyl 9-(3'-thienylmethyl)-fluorene-9-carboxylate* formed clusters of white prisms (76%) from hexane, m.p. 119.5–120.5°. Found: C, 74.99; H, 5.22%. Calc. for  $C_{20}H_{16}O_2S$ : C, 74.99; H, 5.03%.

*Methyl 9-(1'-naphthylmethyl)-fluorene-9-carboxylate\** crystallized as small prisms (73%) from benzene-hexane, m.p. 154–156°. Found: C, 85.36; H, 5.48%. Calc. for  $C_{26}H_{20}O_2$ : C, 85.69; H, 5.53%.

*Methyl 9-(2'-naphthylmethyl)-fluorene-9-carboxylate\** formed small needles (79%) from benzene-hexane, m.p. 189–191°. Found: C, 85.82; H, 5.71%. Calc. for  $C_{26}H_{20}O_2$ : C, 85.69; H, 5.53%.

*Methyl 9-(4'-cyanobutyl)-fluorene-9-carboxylate*

1,4-Dibromobutane, b.p. 63–65° at 5 mm,  $n_D^{21}$  1.5163, was prepared from tetrahydrofuran in 68% yield.

1,4-Dibromobutane (209 g, 0.84 mole) was stirred and boiled under reflux for 6 hours with potassium cyanide (55 g, 0.8 mole), water (65 ml), and ethanol (220 ml). After being diluted with water, the products were isolated with ether and separated by precise fractionation, giving  $\delta$ -bromovaleronitrile (86 g), b.p. 102–103° at 8 mm,  $n_D^{23}$  1.4776.

Prepared in the usual way, *methyl 9-(4'-cyanobutyl)-fluorene-9-carboxylate* crystallized as long white needles (93%) from methanol, m.p. 89–90°. The analytical sample was obtained after two further crystallizations and had a melting point of 90.5–91.0°. Found: C, 79.05; H, 6.74; N, 4.59%. Calc. for  $C_{20}H_{19}NO_2$ : C, 78.66; H, 6.27; N, 4.59%.  $C\equiv N$  stretching band, 2220  $cm^{-1}$ ;  $C=O$  stretching band, 1740  $cm^{-1}$ .

Commercial  $\delta$ -bromovaleronitrile (Sapon Laboratories) gave 63% of the cyano-ester and 31% of a substance insoluble in hot methanol. The latter crystallized from toluene as small colorless needles, m.p. 221.0–221.5°, after three crystallizations. Found: C, 80.64; H, 5.57%. Calc. for  $C_{34}H_{30}O_4$ : C, 81.25; H, 6.02%. It was identified as *dimethyl butane-1,4-di-9'-fluorenyldi-9'-carboxylate* by synthesis from 1,4-dibromobutane (0.56 g, 0.5 mole) and a solution of methyl fluorene-9-carboxylate (1.23 g, 2.2 moles) in methanol

\*Prepared by Mr. R. C. Wilson.

containing sodium methoxide (from sodium, 0.23 g, 2.1 atoms), identity being established by mixed melting point determination and comparison of infrared spectra.

Saponification of the diester in ethylene glycol gave 1,4-(di-9'-fluorenyl)-butane, which crystallized from acetone-methanol as small white needles, m.p. 161.0–161.5°. Found: C, 93.52; H, 6.49%. Calc. for  $C_{30}H_{26}$ : C, 93.22; H, 6.78%.

### Spiro-compounds

*Indan-1-one-2-spiro-9'-fluorene* (IIIa) was prepared as described in the literature (4) in a maximum yield of 67%. Reduction with ethereal lithium aluminum hydride gave indan-1-ol-2-spiro-9'-fluorene (IVa) in almost quantitative yield. It formed prisms from cyclohexane, m.p. 159–160° (lit. m.p. 160° and 168° (dimorphic) (4)). Found: C, 88.27; H, 5.48%. Calc. for  $C_{21}H_{16}O$ : C, 88.74; H, 5.67%.

*1-Chloroindane-2-spiro-9'-fluorene*, prepared by the reaction between the alcohol and thionyl chloride, crystallized from heptane as elongated prisms (77%), m.p. 172–173° with decomposition to 1,2,3,4-dibenzofluorene. The chloride decomposed similarly in boiling 94% formic acid. Found: C, 83.20; H, 4.89%. Calc. for  $C_{21}H_{16}Cl$ : C, 83.30; H, 4.99%.

*1-Acetoxyindane-2-spiro-9'-fluorene*, prepared either by acetylating the alcohol or by the reaction between the chloride and silver acetate in acetic acid, formed colorless prisms from benzene-hexane, m.p. 132–133°. Found: C, 84.66; H, 5.62%. Calc. for  $C_{23}H_{18}O_2$ : C, 84.64; H, 5.56%.

Heating the alcohol (IVa) with twice its weight of phosphorus pentoxide under boiling xylene gave, after 1 hour, 1,2,3,4-dibenzofluorene (94%) which crystallized from heptane as slender white needles, m.p. 162–163°. Oxidation gave 1,2,3,4-dibenzofluorenone, identical with an authentic sample (8).

*1,2,3,4-Tetrahydronaphthalene-1-one-2-spiro-9'-fluorene* (IIIb) was prepared by cyclizing the acid (IIc) (3 g) in dry ether (50 ml) with hydrogen fluoride (150 ml). During 2 days at room temperature most of the solvents evaporated. The neutral product crystallized from cyclohexane as white needles (2.3 g), m.p. 201–202°. Found: C, 89.71; H, 5.32%. Calc. for  $C_{22}H_{16}O$ : C, 89.16; H, 5.44%.

*1-Hydroxy-1,2,3,4-tetrahydronaphthalene-2-spiro-9'-fluorene* (IVb), prepared by reducing the ketone with ethereal lithium aluminum hydride, crystallized from cyclohexane as small colorless blades (91%), m.p. 197.0–197.5°, depressed to 175–180° by the ketone. Found: C, 88.68; H, 6.11%. Calc. for  $C_{22}H_{18}O$ : C, 88.56; H, 6.08%.

*1,2,3,4-Dibenzo-9,10-dihydrophenanthrene* (V). Dehydration of the alcohol (IVb) (2 g) with phosphorus pentoxide under boiling xylene followed by purification over alumina gave a colorless oil (1.5 g) which has failed to crystallize. The 1,3,5-trinitrobenzene adduct separated from methanol as vermilion rods, m.p. 161–162°. Found: C, 67.98; H, 3.72%. Calc. for  $C_{28}H_{18}N_3O_6$ : C, 68.15; H, 3.88%.

Oxidation with chromic acid in acetic acid gave a trace of 1,2,3,4-dibenzophenanthrene-9,10-quinone.

*1,2,3,4-Dibenzophenanthrene* was prepared as follows. Dehydrogenation of the dihydro compound over 10% palladium-on-charcoal at 300° gave an almost quantitative yield of dibenzophenanthrene, which crystallized as white needles from heptane, m.p. 115–116°. Identity was established by comparison with two authentic samples (12,\* 13) and by preparation of the quinone and picrate. The 1,3,5-trinitrobenzene adduct crystallized as slender orange needles from methanol, m.p. 165–166°. Found: C, 68.30; H, 3.64%.

\* Provided by Dr. C. C. Barker.



Calc. for  $C_{28}H_{17}N_3O_6$ : C, 68.43; H, 3.49%. (This derivative has been reported as forming bright yellow needles from benzene, m.p. 167° (13).)

#### *Cleavage of the Spiro-ketones*

The ketone (1 g) was warmed for 30 minutes with a solution of potassium hydroxide (1 g) in industrial alcohol (50 ml) and the acidic product isolated.

*2-(9'-Fluorenylmethyl)-benzoic acid* (VIIa) crystallized as slender needles (85%) from cyclohexane, m.p. 188–189°. Found: C, 83.72; H, 5.61%. Calc. for  $C_{21}H_{16}O_2$ : C, 83.97; H, 5.37% (lit. m.p. 185–186° (14)). The acid chloride ( $SOCl_2$ ) in benzene at 10° reacted with aluminum chloride to reform the spiro-ketone (57%), identified by mixed melting point determination and comparison of infrared spectra.

*2-(2'-(9''-Fluorenyl)-ethyl)-benzoic acid* (VIIb) crystallized from benzene-hexane as colorless blades (81%), m.p. 163–164°. Found: C, 84.21; H, 6.03%. Calc. for  $C_{22}H_{18}O_2$ : C, 84.05; H, 5.77%.

#### *9-Methylphenanthrene*

The reaction between 9-methyl-9-fluorenylmethanol (2) and thionyl chloride gave a semisolid product which would not form a crystalline picrate from ethanol. The reaction with silver acetate in acetic acid was rapid, silver acetate separating. 9-Methylphenanthrene was isolated as its orange picrate (61%, from ethanol), identical with an authentic specimen (2).

#### ACKNOWLEDGMENTS

Some preliminary experiments were carried out at the University of Ottawa during the tenure of a National Research Council of Canada Postdoctorate Fellowship at the University of Ottawa (1954–56), and the author is indebted to Dr. F. A. L. Anet for his interest and helpful suggestions.

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## LIGHT ABSORPTION STUDIES

### PART XVII. THE ULTRAVIOLET ABSORPTION SPECTRA OF CHLOROBENZENES<sup>1</sup>

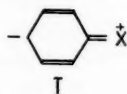
W. F. FORBES<sup>2</sup>

#### ABSTRACT

The ultraviolet absorption spectra of a series of chlorobenzenes are determined. The spectral data suggest that the apparent mesomeric effect of the chlorine atom is greater than that of the fluorine atom, that solvent-solute interactions are generally less important in chlorobenzenes than in fluorobenzenes, and that, as expected, the effective interference radius of the chlorine atom is large. Moreover, spectral changes in *o*-substituted chlorobenzenes are consistent with the assumption that maximum electronic interaction requires the chlorine atom to be in the same plane as the benzene ring. The conformations of *o*-chloroacetophenone and *o*-chlorophenol are briefly discussed.

#### INTRODUCTION

In previous parts of these studies (1), it was found that changes in the location of the so-called *B*-band (for nomenclature employed see refs. 1 and 2) in the ultraviolet spectrum provide a measure of mesomeric interactions;\* that is, spectral changes in the *B*-band could usually be related with changes in the appropriate extended dipolar resonance form of the molecule. For example, the *B*-band of a halogen-substituted benzene can be imagined to owe its existence to the resonance form I, and if this resonance



form is favored, as it is by a number of electron-attracting *p*-substituents, the absorption occurs at longer wavelength and with increased absorption intensity. Other interactions which do not directly affect the resonance form, for example the interactions caused by a *m*-substituent, were found to be only of secondary importance. The *B*-band spectral changes in this way afford a readily available semiquantitative measure of mesomeric interactions as defined above, and generally the information obtained concerning these mesomeric interactions is much as would be expected from simple resonance considerations. One somewhat surprising exception is that for the halogen-substituted benzenes the bathochromic wavelength displacements compared with benzene are in the order iodobenzene > bromobenzene > chlorobenzene > fluorobenzene, and this implies an order of apparent mesomeric interaction  $I > Br > Cl > F$ . This is contrary to the order usually accepted (cf. refs. 1(a), 1(b)).

The *B*-band spectra of the chlorobenzenes are hence of interest and it is the purpose of the present paper to examine, or to re-examine, these spectra assuming that the chlorine atom possesses a greater mesomeric effect, or at least a greater apparent mesomeric effect, than the fluorine atom.

<sup>1</sup>Manuscript received January 25, 1960.

Contribution from the Memorial University of Newfoundland, St. John's, Newfoundland, and the Division of Protein Chemistry, C.S.I.R.O. Wool Research Laboratories, Parkville N.2 (Melbourne), Victoria, Australia.

<sup>2</sup>Present address: Division of Protein Chemistry, C.S.I.R.O., Victoria, Australia.

\*Mesomeric interactions have been defined, for the purpose of this series of papers, as interactions associated with electron mobility acting along systems of conjugated bonds. These mesomeric interactions were found in some instances to be different from the mesomeric interactions as deduced from chemical equilibria (cf. 1(a), 1(b)).

## THE SPECTRUM OF CHLOROBENZENE

The spectra of chlorobenzene in different solvents are listed in Table I.

TABLE I  
Main ultraviolet absorption maxima of chlorobenzene in various solvents

Solvent	B-Band		C-Band	
	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max}$	$\lambda_{\max}$ (m $\mu$ )	$\epsilon_{\max}$
Vapor phase	$\left\{ \begin{array}{l} 211 \\ 215 \\ \text{ca. } 219 \end{array} \right.$	*	$\left\{ \begin{array}{l} 243 \\ 250 \\ 256 \\ 259 \\ 262 \\ 267 \\ 269 \end{array} \right.$	*
Cyclohexane	$\left\{ \begin{array}{l} 211 \\ 215 \\ \text{ca. } 219 \end{array} \right.$	$\left\{ \begin{array}{l} 7500 \\ 7500 \\ 6000 \end{array} \right.$	$\left\{ \begin{array}{l} 245 \\ 251 \\ 257 \\ 261 \\ 264 \\ 271 \end{array} \right.$	$\left\{ \begin{array}{l} 70 \\ 120 \\ 180 \\ 170 \\ 250 \\ 190 \end{array} \right.$
Ether	$\left\{ \begin{array}{l} 211 \\ 214 \\ \text{ca. } 218 \end{array} \right.$	$\left\{ \begin{array}{l} 7000 \\ 7000 \\ 6000 \end{array} \right.$	$\left\{ \begin{array}{l} 244 \\ 250 \\ 257 \\ 264 \\ 271 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \\ 105 \\ 160 \\ 210 \\ 155 \end{array} \right.$
Ethanol	$\left\{ \begin{array}{l} 211 \\ 214 \\ \text{ca. } 218 \end{array} \right.$	$\left\{ \begin{array}{l} 7000 \\ 7000 \\ 5500 \end{array} \right.$	$\left\{ \begin{array}{l} 245 \\ 250 \\ 257 \\ 264 \\ 271 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \\ 110 \\ 160 \\ 200 \\ 140 \end{array} \right.$
Water	$\left\{ \begin{array}{l} 210 \\ 214 \end{array} \right.$	$\left\{ \begin{array}{l} 5000 \\ 4500 \end{array} \right.$	$\left\{ \begin{array}{l} 244 \\ 250 \\ 256 \\ 263 \\ 270 \end{array} \right.$	$\left\{ \begin{array}{l} 65 \\ 100 \\ 135 \\ 165 \\ 115 \end{array} \right.$

NOTE: Values in italics represent inflections in this and the following table.  
\*Intensities not determined.

The similarity of the spectra of fluorobenzene and benzene has been noted in the previous paper (1(a)). This similarity is no longer present between the spectra of chlorobenzene and benzene since the *B*-bands of chlorobenzene, and to a lesser extent the *C*-bands also, are displaced to longer wavelength (see Table I and cf. ref. 1(a)). This spectral change in the *B*-band is related to the increased contributions of resonance forms of type I. That is, it is assumed that at least in the electronic excited state, the chlorine atom is more readily able to interact with the benzene ring than is the fluorine atom.

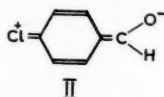
The spectral changes of the chlorobenzene bands with change of solvent are smaller than for fluorobenzene (see Table I and ref. 1(a)). In fact, the only experimentally significant spectral change in the *B*-band is a decreased absorption intensity for the spectrum of chlorobenzene in aqueous solution, which is generally observed for compounds of this type. Particularly interesting is the virtual absence of a wavelength displacement for the *B*-band on determining the spectrum in the vapor phase and in cyclohexane solution ( $\Delta\lambda$  less than 1 m $\mu$ , see Table I), since a number of other compounds examined (3) afford a wavelength displacement appreciably greater than 1 m $\mu$

under these conditions. These observations then suggest that general solvent effects, solvent orientation effects, as well as other solvent-solute interactions such as intermolecular hydrogen bonding, are not important in determining the *B*-band absorption of chlorobenzene.

The *C*-band of chlorobenzene in all solvents is found to be considerably less intense than the *C*-band of fluorobenzene (cf. ref. (1a)).

#### THE SPECTRA OF PARASUBSTITUTED CHLOROBENZENES

Using the simplified concept illustrated by resonance structures of type I, the spectra of *p*-substituted chlorobenzenes can be divided into two groups. (a) First, the group of compounds in which the *p*-substituent is electron-donating, when the *B*-band resembles the *B*-band of the monosubstituted benzene derivative. Of the two substituents, the substituent with the greater electron-donating power will predominantly determine the wavelength and intensity of the monosubstituted benzene *B*-band while the other substituent will exert only a "secondary" effect on the *B*-band. (b) The second group



represents compounds in which the *p*-substituent is electron-withdrawing and resonance interaction is enhanced because of appreciable contributions of resonance forms of type II. These generalizations are illustrated by the data in Table II.

Examination of the data in Table II and of suitable reference compounds shows that generally the *B*-bands of *p*-substituted chlorobenzenes can be identified without undue difficulty. For example, as expected, only one *B*-band, the monochlorobenzene *B*-band, is observed for *p*-dichlorobenzene; somewhat surprisingly, the chlorobenzene *B*-band has been displaced to longer wavelength by about 10  $\mu$  on account of the second chlorine substituent (see Tables I and II). This indicates that the secondary effect of the chlorine atom is such as to favor the transition, and consideration of resonance form I suggests that the second chlorine atom may donate electrons in the electronic excited state and in this way facilitate the transition. Next, the ultraviolet absorption of 1-chloro-4-fluorobenzene has previously been ascribed to chlorobenzene absorption (1(a)), and this again suggests that at least in this compound the chlorine atom possesses the greater mesomeric effect. The only other *B*-band which is associated with chlorobenzene absorption is the band at 221  $\mu$  in *p*-chlorotoluene; this assignment is made because the methyl substituent, like the chloro substituent, would be expected to cause absorption at longer wavelength and because the *C*-band indicates the characteristic chlorobenzene fine structure (see Tables I and II). The *B*-band of the remaining *p*-substituted chlorobenzenes, in which the *p*-substituent is electron-donating, i.e. Br, I, OH, OCH<sub>3</sub>, or NH<sub>2</sub>, is similar to the *B*-band of the corresponding monosubstituted benzene derivative, that is, it is similar to the *B*-band of bromobenzene, iodobenzene, etc.\* Again generally, the *p*-chloro substituent appears to facilitate the absorption since normally the *p*-substituted compound tends to absorb at slightly longer wavelength and with increased

\*It may be noted that *p*-chlorophenol is tentatively assumed to absorb as phenol rather than as chlorobenzene although chlorobenzene absorbs at longer wavelength, that is, the transition involves less energy. However, this apparent anomaly can be explained by the previously made suggestion (1(c)) that the *p*-electrons of the OH-group in phenol are not in the most favorable position for electronic excitation and that because of this, phenol absorbs at unusually short wavelength. It is possible that in *p*-chlorophenol the OH-group tends to twist towards an energetically more favorable position for transition and that consequently the phenol *B*-band absorption is favored.

TABLE II—Main ultraviolet absorption maxima of substituted chlorobenzenes in cyclohexane solution

Substituent	Para isomer			Meta isomer			Ortho isomer		
	B-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	C-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	B-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	2nd B-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	C-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	B-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	2nd B-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	C-Band $\lambda_{\max}$ (m $\mu$ ) $\epsilon_{\max}$	
—Cl	$\left\{ \begin{array}{l} 225 \text{ } 13,500 \\ \text{ca. } 229 \text{ } 10,500 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{ca. } 253 \\ 260 \\ 265 \\ \text{ca. } 268 \end{array} \right\}$	$\left\{ \begin{array}{l} 130 \\ 225 \\ 350 \\ \text{ca. } 268 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 250 \\ 256 \\ 263 \\ 270 \\ 277 \end{array} \right\}$	$\left\{ \begin{array}{l} 216 \\ 219 \\ \text{ca. } 224 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 249 \\ \text{ca. } 255 \\ 261 \\ \text{ca. } 265 \end{array} \right\}$	
—Br	$\left\{ \begin{array}{l} 224 \text{ } 13,500 \\ \text{ca. } 230 \text{ } 10,000 \end{array} \right\}$	$\left\{ \begin{array}{l} 281 \\ 267 \\ 274 \\ 282 \end{array} \right\}$	$\left\{ \begin{array}{l} 450 \\ 250 \\ 340 \\ 415 \\ 335 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{ca. } 212 \text{ } 12,000^* \\ \text{ca. } 218 \text{ } 10,500 \\ \text{ca. } 224 \text{ } 7,000 \\ \text{ca. } 228 \text{ } 5,500 \end{array} \right\}$	$\left\{ \begin{array}{l} 251 \\ 257 \\ 264 \\ 271 \\ 278 \end{array} \right\}$	$\left\{ \begin{array}{l} 216 \\ 219 \\ \text{ca. } 224 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 249 \\ \text{ca. } 255 \\ 261 \\ \text{ca. } 265 \end{array} \right\}$	
—I	$\left\{ \begin{array}{l} 234 \text{ } 18,000 \\ 239 \text{ } 17,500 \end{array} \right\}$	$\left\{ \begin{array}{l} 258 \\ 264 \\ 274 \\ \text{ca. } 286 \end{array} \right\}$	$\left\{ \begin{array}{l} 1,100 \\ 1,000 \\ 750 \\ 375 \end{array} \right\}$	$\left\{ \begin{array}{l} 231 \text{ } 12,000 \\ 236 \text{ } 11,000 \end{array} \right\}$	$\left\{ \begin{array}{l} 252 \\ 258 \\ 266 \\ 274 \end{array} \right\}$	$\left\{ \begin{array}{l} 222 \\ 228 \end{array} \right\}$	$\left\{ \begin{array}{l} 231 \text{ } 10,500 \\ 237 \text{ } 11,000 \end{array} \right\}$	$\left\{ \begin{array}{l} 252 \\ 258 \\ 264 \\ 269 \\ 273 \end{array} \right\}$	
—CH <sub>3</sub>	221 9,000	$\left\{ \begin{array}{l} 244 \\ \text{ca. } 251 \\ 256 \\ 263 \\ 269 \end{array} \right\}$	$\left\{ \begin{array}{l} 100 \\ 160 \\ 240 \\ 370 \\ 500 \end{array} \right\}$	214 8,000	$\left\{ \begin{array}{l} 254 \\ 261 \\ 267 \\ \text{ca. } 271 \end{array} \right\}$	212 8,500	—	$\left\{ \begin{array}{l} 280 \\ \text{ca. } 253 \\ 258 \\ \text{ca. } 262 \\ 266 \end{array} \right\}$	
—OH	224 8,800	$\left\{ \begin{array}{l} 275 \\ \text{ca. } 281 \end{array} \right\}$	$\left\{ \begin{array}{l} 520 \\ 1,400 \\ 1,850 \end{array} \right\}$	216 6,500	$\left\{ \begin{array}{l} 268 \\ 274 \\ 281 \end{array} \right\}$	—	212 6,450*	$\left\{ \begin{array}{l} 268 \\ 274 \\ 281 \end{array} \right\}$	
—OCH <sub>3</sub>	228 11,700	$\left\{ \begin{array}{l} 289 \\ \text{ca. } 276 \end{array} \right\}$	$\left\{ \begin{array}{l} 1,700 \\ 1,400 \end{array} \right\}$	219 7,300	$\left\{ \begin{array}{l} 269 \\ \text{ca. } 275 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 219 \\ 223 \end{array} \right\}$	$\left\{ \begin{array}{l} 281 \\ \text{ca. } 270 \\ 275 \end{array} \right\}$	
—NH <sub>2</sub>	243 12,500	$\left\{ \begin{array}{l} 282 \\ 290 \\ \text{ca. } 291 \end{array} \right\}$	$\left\{ \begin{array}{l} 1,900 \\ 1,850 \\ 1,650 \end{array} \right\}$	238 8,500	$\left\{ \begin{array}{l} 282 \\ 289 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 223 \\ 236 \end{array} \right\}$	$\left\{ \begin{array}{l} 240 \\ 283 \\ 291 \end{array} \right\}$	
—COCH <sub>3</sub>	249 17,000	$\left\{ \begin{array}{l} 297 \\ \text{ca. } 306 \end{array} \right\}$	$\left\{ \begin{array}{l} 1,900 \\ 1,300 \end{array} \right\}$	239 10,000	286 1,100	—	235 5,700	280 650	
—CHO	$\left\{ \begin{array}{l} 253 \text{ } 19,000 \\ 259 \text{ } 15,500 \end{array} \right\}$	$\left\{ \begin{array}{l} 272 \\ 284 \\ 276 \end{array} \right\}$	$\left\{ \begin{array}{l} 900 \\ 500 \\ 1,500 \end{array} \right\}$	$\left\{ \begin{array}{l} 241-242 \\ 248 \end{array} \right\}$	$\left\{ \begin{array}{l} 295 \\ 288 \\ 298 \end{array} \right\}$	—	$\left\{ \begin{array}{l} 246 \\ 252 \end{array} \right\}$	$\left\{ \begin{array}{l} 1,750 \\ 1,400 \\ 1,300 \end{array} \right\}$	
—NO <sub>2</sub>	$\left\{ \begin{array}{l} 214 \text{ } 10,700^* \\ \text{ca. } 219 \text{ } 9,000^* \\ 265 \text{ } 12,000 \\ \text{ca. } 273 \text{ } 11,000 \end{array} \right\}$	$\left\{ \begin{array}{l} \text{ca. } 290 \\ 290 \\ 299 \end{array} \right\}$	$\left\{ \begin{array}{l} 3,000 \\ 2,150 \\ 1,300 \end{array} \right\}$	254 7,800	$\left\{ \begin{array}{l} \text{ca. } 286 \\ 290 \\ 299 \end{array} \right\}$	$\left\{ \begin{array}{l} 210 \\ 216 \\ \text{ca. } 223 \end{array} \right\}$	$\left\{ \begin{array}{l} 244 \\ 244 \end{array} \right\}$	$\left\{ \begin{array}{l} 1,300 \\ 1,300 \\ \text{ca. } 295 \end{array} \right\}$	

\*B-Band assignment doubtful.

absorption intensity compared with the non-chlorosubstituted parent compound. For example, in cyclohexane solution, anisole absorbs maximally at 220  $m\mu$ ,  $\epsilon = 7500$  (1(d)), whereas *p*-chloroanisole absorbs maximally at 228  $m\mu$ ,  $\epsilon = 11,700$  (see Table II).

Although the *p*-chloro substituent, in the examples listed in the last paragraph, gives rise to an appreciable intensity increase, for example, in the anisole *B*-band of chloroanisole, this intensity increase is generally less than if the non-chloro substituent is electron-withdrawing. This is shown by the observed high absorption intensities of the *p*-substituted chlorobenzenes listed towards the end of Table II. This increased transition probability, as well as the generally more pronounced bathochromic wavelength displacement compared with chlorobenzene or compared with the non-chloro-monosubstituted benzene derivatives, suggests resonance structures of type II, since the contribution of resonance forms of type II would be expected, on the basis of our general hypothesis relating resonance interaction and *B*-band absorption, to cause intensified *B*-band absorption occurring at longer wavelength. In this way, the *B*-bands of these *p*-substituted chlorobenzenes are associated, at least partly, with resonance structures involving the *entire* molecule, whereas the *B*-bands of the previously mentioned *p*-substituted chlorobenzenes are associated with resonance structures involving, as a first approximation, only *part* of the molecule; that is, they are associated with transitions involving predominantly so-called locally excited states.

#### THE SPECTRA OF METASUBSTITUTED CHLOROBENZENES

The frequent occurrence of two *B*-bands in the spectra of *m*-disubstituted benzene derivatives has previously been noted and may be rationalized in terms of simple resonance theory. That is, resonance forms of type I will not normally be greatly affected by a *m*-substituent and thus the *B*-band of the *m*-disubstituted compound will resemble the *B*-band of one of the monosubstituted parent compounds. Moreover, if electrons are highly localized in both substituent groups, two *B*-bands corresponding to both monosubstituted parent compounds can apparently sometimes be identified (see refs. 1(c), 1(d), 1(e)).

For *m*-substituted chlorobenzenes therefore the chlorobenzene *B*-band would be expected to occur near 215  $m\mu$  (see Table I), that is, at a location at which it cannot always be identified with certainty since *A*-band absorption (cf. ref. 2) also frequently occurs near this wavelength. However, in compounds like *m*-dichlorobenzene, the band near 220  $m\mu$  evidently represents the chlorobenzene *B*-band, and the bands near 225  $m\mu$  in *m*-chloriodobenzene and near 215  $m\mu$  in *m*-chlorotoluene are also tentatively ascribed to chlorobenzene *B*-band absorption (see Table II). In all these examples the second substituent, if electron-donating, facilitates the chlorobenzene *B*-band absorption, apparently in a less pronounced, though presumably similar, manner as has been postulated for the corresponding *p*-isomers. If the second substituent is electron-withdrawing, as for example in *m*-chloronitrobenzene, the reverse effect is tentatively assumed to occur since the chlorobenzene *B*-band appears to be displaced to *shorter* wavelength and probably occurs near 210  $m\mu$ . This, unfortunately, is at a wavelength at which it can no longer be identified with certainty because of possible *A*-band absorption (see Table II).

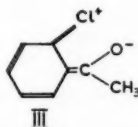
The effect of the *m*-chloro substituent on the *B*-band, associated with the non-chloro-monosubstituted benzene derivative, appears generally to be small and is certainly smaller than the effect of the *p*-chloro substituent. Usually, a small bathochromic



wavelength displacement is observed on account of the *m*-chloro substituent, but sometimes the *B*-band absorption maxima are almost identical. For example, anisole in cyclohexane solution absorbs maximally at 220  $m\mu$ ,  $\epsilon = 7500$  (1(*d*)) whereas *m*-chloroanisole under identical conditions absorbs maximally at 219  $m\mu$ ,  $\epsilon = 7300$  (see Table II). Or, benzaldehyde in hexane solution absorbs maximally at 241  $m\mu$ ,  $\epsilon = 14,000$  whereas *m*-chlorobenzaldehyde under similar conditions absorbs maximally at 241–242  $m\mu$ ,  $\epsilon = 11,500$  (1(*e*)). It may be noted that a related effect has also been reported for some of the infrared data. For example, the location of the hydroxyl band in phenol at 3608  $cm^{-1}$  is reported close to the hydroxyl band in *m*-chlorophenol (3607  $cm^{-1}$ ;  $A = 6.7 \times 10^{-7}$ ); the band is, however, slightly enhanced compared with the intensity of the corresponding phenol band ( $A = 5.8 \times 10^{-7}$ ) (4).

#### THE SPECTRA OF ORTHOSUBSTITUTED CHLOROBENZENES

The *B*-bands of *o*-substituted chlorobenzenes generally resemble the *B*-bands of the corresponding meta isomers. In terms of canonical resonance forms this suggests that dipolar excited states of type III are not important in determining the *B*-band. This may



be because of steric considerations, that is, because the two substituents are not sufficiently coplanar for effective resonance interaction to occur, or it may be because the molecule inherently absorbs by means of transitions involving predominantly locally excited states. For example, if the non-chloro substituent is electron-donating, as in *o*-chlorophenol, *o*-chloroaniline, etc., dipolar resonance forms of type III may be neglected and *B*-bands associated with locally excited states, that is phenol and aniline *B*-bands would be expected and are in fact observed (see Table II).<sup>\*</sup> For *o*-substituted chlorobenzenes, however, in which the non-chloro substituent is electron-withdrawing, the steric hypothesis is favored since if the non-chloro substituent is relatively small, as in *o*-chlorobenzaldehyde, there is observed a slight bathochromic wavelength displacement relative to the *B*-band in the meta isomer, indicative of resonance interaction of type III; in *o*-chloroacetophenone and *o*-chloronitrobenzene on the other hand, no such bathochromic wavelength displacement is observed and this therefore suggests that only in *o*-chlorobenzaldehyde are the two *o*-substituents in the same plane.

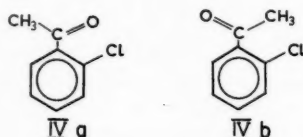
Since the benzaldehyde, nitrobenzene, and acetophenone absorption is still readily discerned (see Table II) in the spectra of the *o*-chlorosubstituted compounds and since, moreover, there is quite generally a similarity between the spectra of ortho and meta isomers in compounds of this type, this suggests that non-planarity is caused, at least partly, at the expense of the chlorine atom. Hence it may tentatively be assumed that not only are the formyl, acetyl, or nitro groups twisted out of the plane of the benzene ring but also that the chlorine atom is bent away from the plane of the benzene ring,

<sup>\*</sup>In some *o*-substituted chlorobenzenes, such as *o*-chloroanisole, it is possible that the observed *B*-band corresponds, at least partly, to chlorobenzene *B*-band absorption. However, the present spectral evidence, for example, the spectral changes observed on altering the solvent for *o*-chloroanisole which closely resemble the solvent changes observed for anisole (3) do not favor this possibility, nor do the infrared data (see Experimental).

and it may be because of this bending away that the chlorine atom is frequently no longer able to interact effectively with the benzene ring in the manner required to give rise to resonance interaction as shown in structure III.

Although the precise relation between steric interactions and spectral effects in *o*-substituted chlorobenzenes is evidently not entirely clear, some form of steric interaction in a number of *o*-substituted chlorobenzenes is indicated by the pronounced intensity decreases in the *B*-bands of compounds like *o*-chloroacetophenone and *o*-chloronitrobenzene compared with the intensities for the corresponding meta isomers or compared with the *B*-band intensities of the corresponding non-chloromonosubstituted benzene derivatives (see Table II and ref. 1). The intensity decrease in these *o*-substituted chlorobenzenes is greater than in the corresponding methylacetophenones (1(f)) or methylnitrobenzenes (1(g)), and this suggests that the effective interference radius of the chlorine atom is greater than that of the methyl group. On the other hand, the reported spectra of the *o*-chloro- and *o*-methyl-acetanilides (5), for example, suggest an opposite order. However, even then the observed intensity decrease in the *B*-band of the *o*-chloro compound is appreciable, and this then at least confirms the belief that the effective interference radius of the chlorine atom is large. The present data, as well as other related data, hence clearly indicate the presence of appreciable steric interactions caused by an *o*-chloro substituent (6, 7, 8). (Indications that the chlorine atom, when attached to a benzene ring, causes appreciable steric interactions are also provided by the postulated puckered nature of the benzene ring in hexachlorobenzene (9).)

Concerning the actual conformation of a compound like *o*-chloroacetophenone, the infrared carbonyl band shows a doublet which has been assumed to indicate that *o*-chloroacetophenone exists in two *s-cis*, *s-trans* conformations IVa and IVb, with IVb

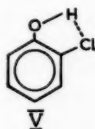


representing the slightly more stable conformation (10).<sup>\*</sup> Because of electrostatic and steric considerations, it seems unlikely that either of these conformations should be entirely coplanar, and this observation relates well with the low intensity of the *B*-band in the ultraviolet region, which indicates non-planarity of the molecule. On the other hand, the acetyl group must be, at least partly, coplanar with the benzene ring because the characteristic acetophenone maximal absorption near 235  $\mu$  is still evident in *o*-chloroacetophenone (see Table I). The most probable explanation consistent with all the above-mentioned observations seems to be that *o*-chloroacetophenone exists in at least two conformations, most of them not entirely coplanar, with the preferred angle between the plane of the nitro group and that of the C—Cl bond being very approximately 30°.

The spectral data discussed above suggest the operation of steric interactions in a number of *o*-substituted chlorobenzenes. On the other hand, neither *B*-band nor *C*-band

<sup>\*</sup>Two *s-cis*, *s-trans* conformations have also been postulated for *o*-chloroanisole (11) on the basis of a doublet in the ultraviolet region. However, doublets are frequently observed in the ultraviolet region, even if no *s-cis*, *s-trans* isomerism is possible (cf., for example, the observed doublet in the ultraviolet spectrum of benzaldehyde (1(e)). Further, no evidence for two conformations, in the form of doublets, has been obtained for the infrared spectrum of *o*-chloroanisole (see Experimental), and Banerjee's hypothesis is therefore not favored.

data provide any convincing evidence for the existence of an intramolecular hydrogen bond as has frequently been postulated for compounds like *o*-chlorophenol (V). (For



recent discussions concerning this type of intramolecular hydrogen bonding see refs. 12, 13, 14, 15, 16.) That is, comparing the spectra of *o*- and *m*-chlorophenol, no bathochromic wavelength displacements are observed in the *B*- and *C*-bands of the *o*-isomer, the  $\epsilon_{\max}$  value of the *B*-band in the *o*-isomer is not greater than the corresponding  $\epsilon_{\max}$  value in the *m*-isomer, and the  $\epsilon_{\max}$  value of the *C*-band in the *o*-isomer, although slightly larger than for the *m*-isomer, is not large as for *o*-chloroanisole and, moreover, the increase in  $\epsilon_{\max}$  values between ortho and meta isomers are comparable for chlorophenols and chloroanisoles (see Table II). Further, *o*-chlorophenol in ethanolic solution absorbs as follows:  $\lambda_{\max}$  216 m $\mu$ ,  $\epsilon$  = 6400;  $\lambda_{\max}$  276.5 m $\mu$ ,  $\epsilon$  = 2350; and  $\lambda_{\text{infl}}$  ca. 280 m $\mu$ ,  $\epsilon$  = 2000; and in ether solution *o*-chlorophenol absorbs as follows:  $\lambda_{\max}$  217 m $\mu$ ,  $\epsilon$  = 6200;  $\lambda_{\max}$  275 m $\mu$ ,  $\epsilon$  = 2400; and  $\lambda_{\text{infl}}$  ca. 281 m $\mu$ ,  $\epsilon$  = 2000; these spectra are appreciably different from the absorption spectrum of *o*-chlorophenol in cyclohexane solution (see Table II). Since an intramolecular hydrogen bond in *o*-chlorophenol would be expected to cause bathochromic wavelength displacements in both *B*- and *C*-bands accompanied by intensity increases, and since, further, the spectrum of an intramolecular hydrogen-bonded compound would not be unduly affected by solvent changes, the ultraviolet data point against the presence of structures of type V for solutions of *o*-chlorophenol in ethanol or ether solutions and to a lesser extent to the absence of such structures also in cyclohexane solution.

#### EXPERIMENTAL

The ultraviolet absorption spectra were determined by standard methods in 1-cm cells using a Unicam SP500 spectrophotometer calibrated against a didymium filter. For each compound at least two independent sets of observations were made. The accuracy of  $\lambda_{\max}$  values is estimated to be  $\pm 2$  m $\mu$ , and the precision of  $\epsilon_{\max}$  values  $\pm 5\%$  or better. Values of  $\epsilon_{\max}$  were reproducible in most cases to  $\pm 2\%$ . The ultraviolet data are listed in Tables I and II and in the discussion of *o*-chlorophenol. Some of the spectra have previously been described in this series and elsewhere. Whenever possible, the chlorobenzene spectra were determined under conditions identical with those under which previous spectra in this series had been determined. Frequently, but not always, the data were in good agreement with recent values reported by other workers (cf. for example, ref. 17).

The infrared spectra were determined on a Unicam SP100 instrument, using a NaCl prism and a diffraction grating.

The infrared spectrum of *o*-chloroanisole was determined in the liquid phase in the region 650–2000  $\text{cm}^{-1}$  and was found to be more like the infrared spectrum of anisole than the infrared spectrum of chlorobenzene under identical conditions. No evidence in the way of doublet formation, for two different conformations, could be detected for the infrared spectrum of *o*-chloroanisole within this region.

The chlorobenzenes were mostly commercial materials, purified by distillation or recrystallization until their boiling points and refractive indices or melting points showed them to be sufficiently pure. The solvents used were spectroanalyzed cyclohexane (Fisher) or other commercially available spectroanalyzed solvents.

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# DISINTEGRATION-RATE DETERMINATION BY $4\pi$ -COUNTING

## PART V. FURTHER STUDIES ON ABSORPTION AND SCATTERING OF $\beta$ -RADIATION<sup>1</sup>

L. YAFFE AND J. B. FISHMAN<sup>2,3</sup>

### ABSTRACT

The work of Pate and Yaffe on the study of absorption and scattering of  $\beta$ -radiation in a  $4\pi$ -counter has been extended to greater source-mount thickness. As the thickness is increased, the backscattering curves assume the juxtaposition obtained in  $<2\pi$  geometrical systems. The saturation backscattering value  $S$  is attained at a mass approximately one-fifth that of the range of the  $\beta$ -radiation. The relationship  $S = 0.070 \log_{10} E_{\max} + 0.142$ , where  $E_{\max}$  is the maximum energy of the  $\beta$ -radiation, is obeyed over the range studied. The phenomenon of coincident discharges, while adequately explained by Pate and Yaffe as caused by wall- and gas-scattering if thin film source mounts are used, cannot completely account for the results with thicker films. Other phenomena, such as bremsstrahlung and secondary electron production, begin to play a role.

### INTRODUCTION

Previous publications in this series (1, 2, 3, 4, 5) have described experimental work aimed at improving the accuracy of determination of disintegration rates using a  $4\pi$   $\beta$ -proportional counter. In one of these papers (4) Pate and Yaffe studied some of the scattering and absorption processes involved in a  $4\pi$  steradian geometrical arrangement.

Normally, when the disintegration rate is to be determined, a sample is evaporated on a thin film and placed between two half-counters, the anodes of which are connected in parallel. It has been found by some workers that 'coincident' discharges occur in such an arrangement, i.e. both halves of the counter are discharged within the resolving time of the apparatus by a single disintegration. Pate and Yaffe attempted to fix the cause of these coincidences, in addition to studying the absorption and scattering of the radiation by the source-mounting film.

They have shown that if one uses thin films, of the order of a few hundred micrograms per square centimeter or less, these coincidences are due to backscattering of the radiation from the counter gas and counter walls. The frequency of occurrence of these discharges (as high as 20% of the disintegration rates of pure  $\beta$ -emitters even with very thin source mounts) allowed them to eliminate many other suggested causes of this phenomenon. Of those eliminated, only the possible production of secondary electrons, resulting from interaction between the incident  $\beta$ -radiation and the source-mounting film, will be enhanced by the thicker films used in this later study. For simplicity this is omitted in the ensuing treatment.

Following Pate and Yaffe (4) one can set up a simple model for the absorption and scattering processes which occur in a  $4\pi$ -counter.

If both half-counter anodes are connected in parallel, then

$$[1] \quad N_t = N_a + N_b - N_c$$

where  $N_t$  is the total counting rate,  $N_a$  and  $N_b$  are the half-counter rates, and  $N_c$  the coincidence rate.

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Contribution from the Radiochemistry Laboratory, Department of Chemistry, McGill University, Montreal, Que., with financial assistance from the National Research Council of Canada.

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Pate and Yaffe showed that the following relationship held:

$$[2] \quad N_a = \frac{1}{2}N_0[(1+P_2)+P_1P_5P_6]$$

$$[3] \quad N_b = \frac{1}{2}N_0[(1-P_2)P_1+P_5P_6]$$

$$[4] \quad N_c = \frac{1}{2}N_0(P_5P_6+P_1P_5P_6)$$

where  $N_0$  = disintegration rate of the active sample,

$P_1$  = transmission of the film to incident  $\beta$ -radiation from the source,

$P_2$  = the probability that  $\beta$ -radiation originally emitted in the direction of one of the counter halves will be scattered by the film so as to enter the opposite counter half,

$P_5$  = the transmission of the film to backscattered radiation arising from wall and gas backscattering, and

$P_6$  = the probability that the  $\beta$ -radiation incident into either hemisphere is back-scattered by the counter gas and/or counter walls so as to enter the other hemisphere ( $= P_3+P_4$  as defined by Pate and Yaffe).

Values of  $P_6$  were determined by Pate and Yaffe from experiments in which the coincidence rate between the two half-counters was measured with different counter gases and varying aperture sizes. They also obtained values of  $N_a$ ,  $N_b$ , and  $N_c$  for a range of values of  $E$ , the maximum energy of the  $\beta$ -radiation, and  $d$ , the superficial density of the source mount. This enabled them to solve equations [2], [3], and [4] simultaneously and thus determine  $P_1$ ,  $P_2$ , and  $P_5$ . Their results are being extended in this paper to greater source-mount superficial densities.

#### EXPERIMENTAL AND RESULTS

The  $\beta$ -emitters used were  $\text{Ni}^{63}$ ,  $\text{S}^{35}$ ,  $\text{Tl}^{204}$ , and  $\text{P}^{32}$ . This gave a range of maximum energies of the  $\beta$ -radiation from 0.067 to 1.70 Mev. These nuclides were available in solutions which were either 'carrier-free' or of such a high specific activity that evaporation of a suitable aliquot produced a weightless point source on a thin gold-coated VYNS film (1) of superficial density 5–10  $\mu\text{g}/\text{cm}^2$ , mounted on an aluminum ring of 2.5 cm diameter. The source mount was built up by laminating calibrated VYNS films on to the original source mount on the side opposite to that on which the active nuclide had been deposited. This was repeated until the total superficial density was of the order of 1  $\text{mg}/\text{cm}^2$ .

Since the thickest film conveniently produced by the method previously described is only about 20  $\mu\text{g}/\text{cm}^2$ , a different procedure was adopted for producing thicker films. The VYNS resin was dissolved in acetone and the solution poured into plane-bottom dishes floating on mercury. The acetone was allowed to evaporate slowly, the resultant film was peeled off and mounted on a ring. In this way uniform films of superficial densities up to 60  $\text{mg}/\text{cm}^2$  were obtained. The thicker films were rendered conducting by coating them with an evaporated film of gold. They were then placed temporarily in direct contact with the underside of the source-mount films to give a range of film thicknesses above the 1  $\text{mg}/\text{cm}^2$  region.

The  $4\pi$   $\beta$ -proportional gas counter was identical with that described previously. Each anode was operated as a separate unit so that individual half-counter rates and coincidence rates could be determined. Performance of each unit was carefully matched using the threshold of the plateau obtained with  $\text{Ni}^{63}$  as a criterion. Corrections were made for random coincidences as described in the previous paper.



$N_a$ ,  $N_b$ , and  $N_c$  were determined for the series of  $\beta^-$ -emitters over a range of source-mount superficial densities. The total counting rate  $N_t$ , obtained from equation [1], was checked periodically against the counting rate obtained with both anodes connected in parallel.

The results obtained by plotting  $N_a$ ,  $N_b$ ,  $N_c$ , and  $N_t$  against the superficial density of the source mount are shown in Figs. 1-4 inclusive. The values of  $P_1$  and  $P_2$ , obtained for the various nuclides, are shown in Figs. 5 and 6. The former shows data obtained with superficial densities up to 1 mg/cm<sup>2</sup>, while the latter gives data to over 200 mg/cm<sup>2</sup>.

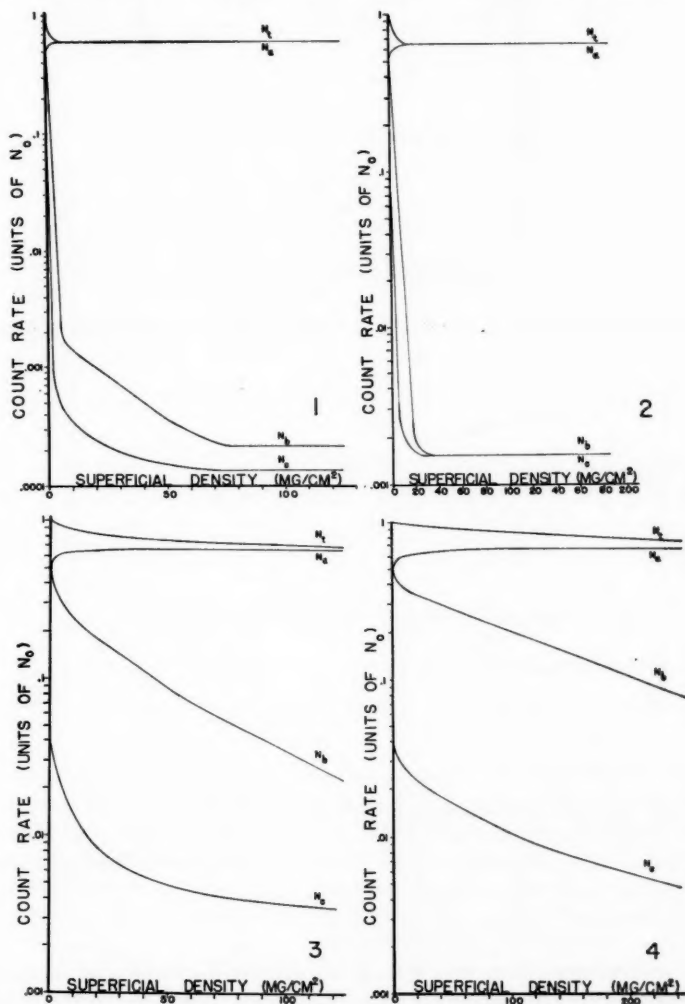


FIG. 1. Variation of  $N_a$ ,  $N_b$ ,  $N_c$ , and  $N_t$  with increase in superficial density of source mount for  $Ni^{60}$ .  
 FIG. 2. Variation of  $N_a$ ,  $N_b$ ,  $N_c$ , and  $N_t$  with increase in superficial density of source mount for  $S^{35}$ .  
 FIG. 3. Variation of  $N_a$ ,  $N_b$ ,  $N_c$ , and  $N_t$  with increase in superficial density of source mount for  $Tl^{204}$ .  
 FIG. 4. Variation of  $N_a$ ,  $N_b$ ,  $N_c$ , and  $N_t$  with increase in superficial density of source mount for  $P^{32}$ .

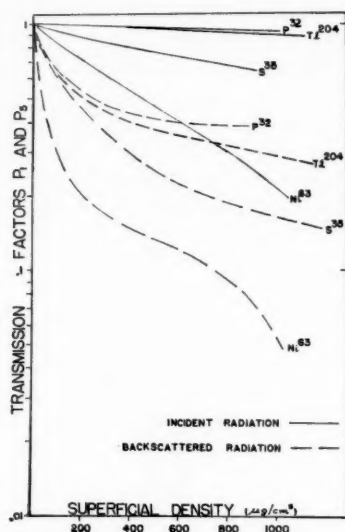


FIG. 5. Variation of transmission factors  $P_1$  and  $P_3$  with increasing superficial density of source mount (to  $1 \text{ mg}/\text{cm}^2$ ).

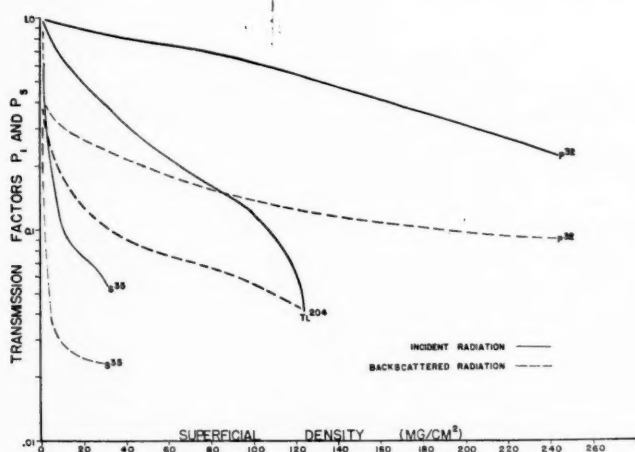


FIG. 6. Variation of transmission factors  $P_1$  and  $P_3$  with increasing superficial density of source mount (to  $60 \text{ mg}/\text{cm}^2$ ).

#### DISCUSSION

For small film thicknesses, less than  $600 \mu\text{g}/\text{cm}^2$ , the backscattering data are essentially similar to those of Pate and Yaffe (4), and are shown in Fig. 7. However, the backscattering coefficients are somewhat lower, due possibly to the smaller amount of gold coating on the VYNS films in this series of experiments. As the film thickness increases above the range employed by Pate and Yaffe, as shown in Fig. 8, the curves assume the

juxtaposition similar to those obtained in  $<2\pi$  geometrical arrangements (6, 7, 8), i.e. that nuclide with  $\beta$ -radiation of greatest maximum energy has the greatest backscattering factor.

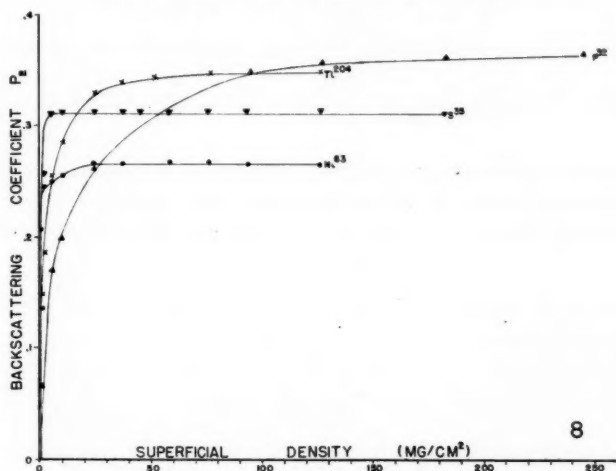
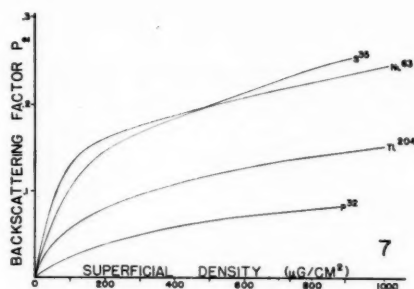


FIG. 7. Variation of the backscattering factor  $P_2$  with increasing superficial density of source mount (to 1 mg/cm<sup>2</sup>).

FIG. 8. Variation of the backscattering factor  $P_2$  with increasing superficial density of source mount (to 250 mg/cm<sup>2</sup>).

In Fig. 9 is shown the entire range on a logarithmic plot. The range of the  $\beta$ -radiation is indicated and, as in the case of  $<2\pi$  geometrical systems, saturation backscattering is obtained with approximately that amount of material corresponding to about one-fifth the range of the  $\beta$ -radiation.

One can clearly note the transition from the single scattering events, observed with thin films, to the region of multiple scattering. The single scattering events involve electrons incident at small angles to the film and will be greatest for small electron energies as shown in Fig. 7. The behavior of this type of scattering has been described by McKinley and Feshbach (9) amongst others. As the film thickness increases the intermediate region of 'plural' scattering is encountered. The effect of  $\beta$  end-point energy is very pronounced in this region. With Ni<sup>63</sup>, for example, the backscattering coefficient rises very rapidly and then attains a maximum value characteristic of the electron diffusion

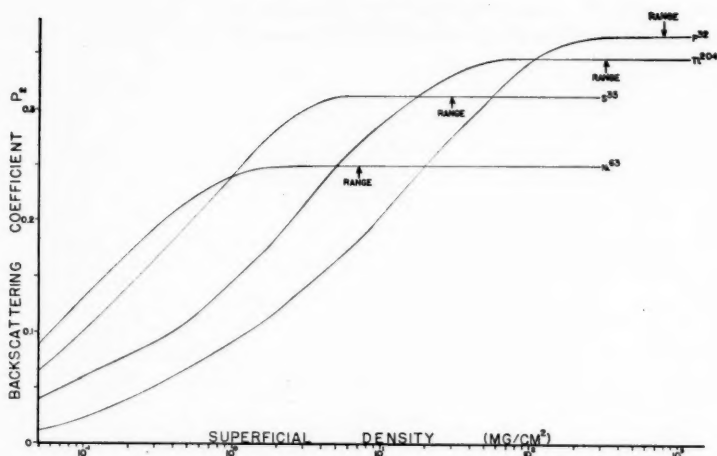


FIG. 9. Variation of the backscattering factor  $P_2$  with the logarithm of the superficial density of the source mount.

type characterized as 'multiple' scattering. For  $P^{32}$ , however, the rise is gradual and the rate of change of slope to the maximum backscattering value is very much less than for  $Ni^{63}$ . The greater the  $\beta$  end-point energy, the greater is the region of 'plural' scattering.

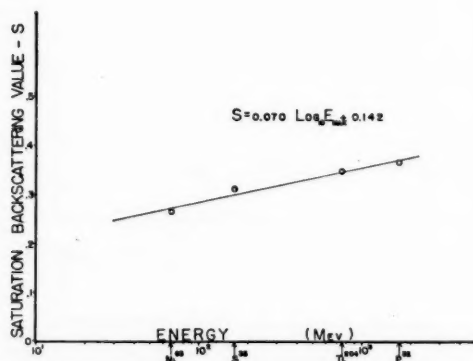


FIG. 10. Variation of the saturation backscattering value with the logarithm of the maximum energy of the  $\beta$ -emitter.

In Fig. 10 is shown the saturation backscattering value  $S$  plotted against the logarithm of the maximum energy of the  $\beta$ -radiation. This is essentially linear and follows the empirical equation

$$S = 0.070 \log_{10} E_{\max} + 0.142.$$

The saturation backscattering factors found were much larger than those obtained in arrangements with much smaller geometrical efficiency. These are shown in Fig. 11,

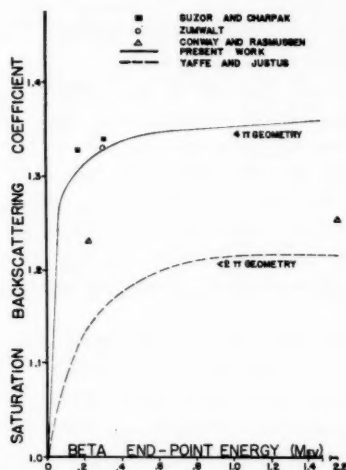


FIG. 11. Variation of saturation backscattering coefficient with  $\beta^-$  end-point energy.

together with extrapolated data for systems of  $<2\pi$  geometrical efficiency of Yaffe and Justus (7) and Burtt (10) for saturation backscattering with backing material of mean atomic number  $\bar{Z} = 11.2$ , the mean atomic number of the VYNS film employed, where

$$\bar{Z} = (\sum_i n_i Z_i^2) / (\sum_i n_i Z_i).$$

Cooper and Yaffe (11) have shown that the above formulation gives the effective mean  $\bar{Z}$  for backscattering by a compound where  $n_i$  refers to the number of atoms of an element of atomic number  $Z_i$  in the compound. The results in Fig. 11 agree with those of other workers who found that the backscattering effect is greater, the greater the geometrical efficiency of the detection system (6, 12, 13, 14).

The increased backscattering coefficient is undoubtedly due to the detection in windowless  $2\pi$ - or  $4\pi$ -counters of backscattered radiation degraded too much in energy to pass through the window of a Geiger tube. The extent of energy degradation is evident from Figs. 5 and 6, from the previous work by Pate and Yaffe (4), and the observation by Balfour (15) of a large portion of low-energy rays in the spectrum of backscattered radiation. Another reason why some of these low-energy backscattered particles miss detection in small geometry systems is the fact, ascertained by Brownell (16), that the average energy for backscattered radiation varies with the angle of scattering, with a greater amount of particles having a lower average energy at low scattering angles.

Published data dealing with saturation backscattering coefficients in windowless counters of geometrical systems of  $2\pi$  or greater are very sparse, so that comparison with present results is very difficult. Suzor and Charpak (17) obtained saturation backscattering coefficients for  $S^{35}$  and  $Co^{60}$  with aluminum in a  $4\pi$ -counter. However, since they used the 'sandwich' technique for determining the absolute disintegration rates, their results are slightly in error (4). Their values are shown in Fig. 11 for comparison. Zumwalt's (6) values for  $Co^{60}$  in a  $2\pi$ -counter, extrapolated to  $\bar{Z} = 11.2$ , are also shown for comparison. Conway and Rasmussen's (14) values for  $Pm^{147}$  and  $Sr^{90}$ - $Y^{90}$ , determined in a  $2\pi$ -counter, included in the same diagram, are much lower than ours or those of Zumwalt.

Christian *et al.* (18) determined backscattering coefficients for  $\text{Ni}^{63}$ ,  $\text{Co}^{60}$ ,  $\text{P}^{32}$ , and  $\text{S}^{35}$  in a  $2\pi$ -counter. Their value for  $\text{Ni}^{63}$  corresponds well with ours. However, their other points seem too erratic and unsystematic to be very useful.

If one examines equations [2], [3], and [4], it is apparent that, as  $d$ , the thickness of film, increases beyond the range of the backscattered and incident  $\beta$ -radiation, then  $P_s$  and  $P_i$  approach zero. This would mean that  $N_b$  and  $N_e$  would approach zero. Examination of Figs. 1-4 shows that the curves do not reach zero, but level off (as is shown markedly in the case of the weaker  $\beta$ -emitters). It seems obvious then that the assumptions made in the derivation of the above equations, i.e. that the only processes causing coincidences are counter wall- and gas-scattering, are only approximate. As the film thickness is increased other phenomena, such as bremsstrahlung or secondary electron production, begin to play a role.

It has been shown by Bolgiano *et al.* (19) that the probability of inner bremsstrahlung production is in the order of  $10^{-4}$ . Thus, coupled with the low probability for detection of photons in the  $4\pi$ -counter, this process will contribute very little.

The radiation from external bremsstrahlung has a maximum photon energy equal to the energy of the  $\beta$ -radiation and an intensity proportional to the mean atomic number of the absorbing material. It has been shown (20) that the fraction of the  $\beta$ -energy, which appears as external bremsstrahlung, is given approximately by  $\bar{Z}E_{\text{max}}/3000$ . For VYNS and  $\text{P}^{32}$  this amounts to about 0.5%. As before, this low probability and the low probability of photon detection would only contribute a small amount to the coincidences taking place.

This then leaves secondary electron production. Their liberation by the photoelectric effect may again be ignored owing to the low probability, of the order of  $10^{-4}$ . However, if an electron of initial energy  $E$  produces by collision two electrons of energy  $W$  and  $E-W$ , then Mott (21) has shown that the number of secondary electrons,  $I$ , produced in a distance  $dx$ , in the energy range  $W$  to  $W-dW$  is

$$[5] \quad I = \bar{Z}N dx d\phi(E, W)$$

where  $\bar{Z}$  is the mean atomic number of the stopping material and  $N$  the number of atoms per square centimeter of the stopping material.

The differential scattering cross section  $d\phi(E, W)$  has been determined by Page (22). He found that, for  $\beta$ -radiation between 0.6 and 1.7 Mev, the value of  $d\phi(E, W)$  in collision was of the order of  $10^{-24} \text{ cm}^2$ . If this value is substituted into equation [5], taking  $\bar{Z} = 11.2$ ,  $N \approx 10^{23}$ , and  $dx \approx 0.1 \text{ cm}$ , then  $I = 0.10$ . This is now a reasonably high probability, so that this process can no longer be ignored since every electron produced will be detected.

This, of course, cannot account for the 'coincident discharge' with films of thickness greater than the range of the original  $\beta$ -radiation, e.g. in the case of  $\text{Ni}^{63}$ . In these instances, the discharges must be due to a combination of causes which could include bremsstrahlung from the counter gas and walls, the bremsstrahlung discussed above, and perhaps a small contribution from a hard cosmic ray component which would trigger both counters contributing to the coincidences.

Pate and Yaffe (3) have determined the absorption parameter ( $N_T/N_0$ ) as a function of  $\beta$  end-point energy for a series of film thicknesses. This is shown in Fig. 3 in their paper. These data have been extended, as shown in Fig. 12 of this paper, to lower energies with the inclusion of results obtained by the study of  $\text{H}^3$  ( $E_{\text{max}} = .018 \text{ Mev}$ ). The added data fall into place in very satisfactory fashion.



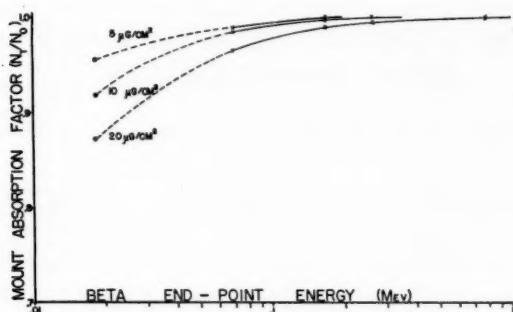


FIG. 12. Absorption parameter ( $N_T/N_0$ ) as a function of  $\beta$  end-point energy. The data of Pate and Yaffe (3) are extended to lower end-point energies.

#### ACKNOWLEDGMENTS

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## THE REACTION OF SULPHURYL CHLORIDE WITH GLYCOSIDES AND SUGAR ALCOHOLS. PART II<sup>1</sup>

J. K. N. JONES, M. B. PERRY, AND J. C. TURNER

### ABSTRACT

The structures of methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-hexoside and methyl "4-chloro-4-deoxy- $\beta$ -pentoside" (I) have been investigated. The desulphation reaction leading to the formation of the latter compound is described. Replacement of the hydroxyl group at C<sub>(4)</sub> by a chlorine atom in both compounds is shown to have occurred with inversion of configuration.

### INTRODUCTION

In Part I (1) the product of the reaction of sulphuryl chloride with methyl  $\alpha$ -D-glucopyranoside was shown to be probably methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-hexoside 2,3-sulphate which on desulphation gave methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-hexoside (I). It was possible that the replacement of the hydroxyl group at C<sub>(4)</sub> by the chlorine atom had occurred with inversion of configuration to give the galactose configuration.

This problem was investigated using a synthetic route to a methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-hexoside of known configuration. Methyl 4-chloro-4-deoxy- $\alpha$ -D-glucopyranoside was synthesized by the method of Buchanan (2). Reaction with sulphuryl chloride and subsequent desulphation gave a complex mixture from which was isolated methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-glucopyranoside (II) which was found to be different from that obtained from the reaction of sulphuryl chloride with methyl  $\alpha$ -D-glucopyranoside (1). It was found that II consumed periodate extremely slowly (1.04 moles, 167 hours) and this bore some resemblance to the parent methyl 4-chloro-4-deoxy- $\alpha$ -D-glucopyranoside which was oxidized under somewhat similar conditions (1.03 moles, 170 hours) (3, 3a). Accordingly the chlorine atom at C<sub>(4)</sub> of I was placed in the galactose configuration since this was the only position in which I and II differed.

Further evidence as to the configuration at C<sub>(4)</sub> of I was obtained when the reaction of sulphuryl chloride with methyl  $\alpha$ -D-galactopyranoside was examined. Desulphation of the fully substituted product gave a complex mixture from which was isolated a methyl dichloro-dideoxy- $\alpha$ -D-hexoside identical with II.

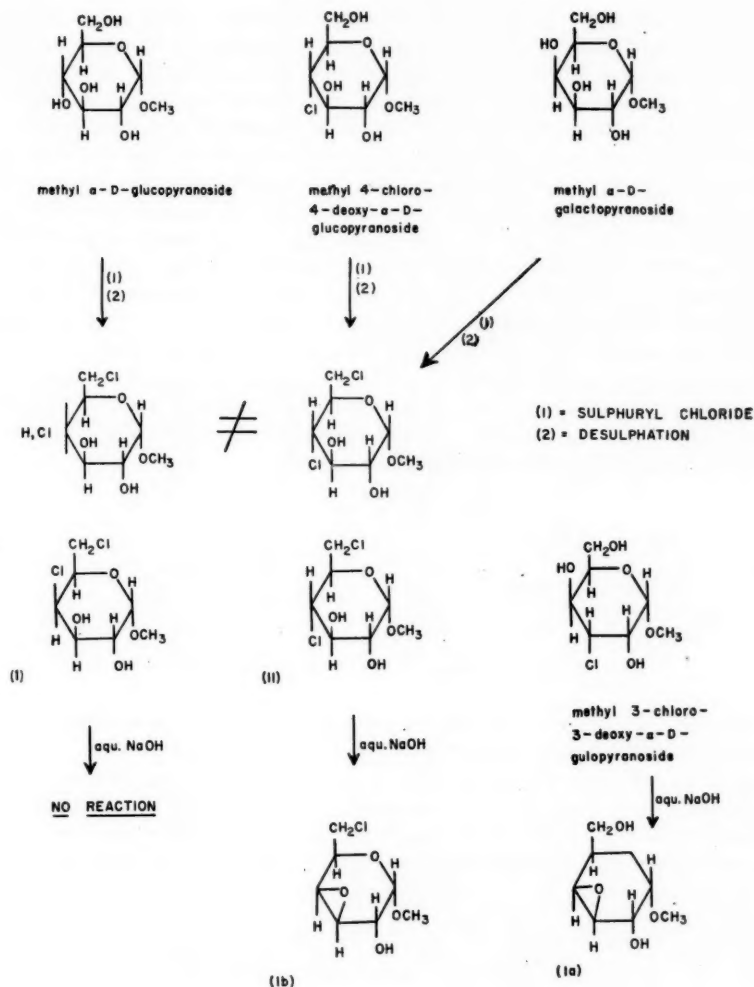
Compound I did not react with sodium hydroxide, whereas II lost approximately 1 equivalent of chlorine under the same conditions probably to give Ib. It was found that methyl 3-chloro-3-deoxy- $\alpha$ -D-gulopyranoside, with sodium hydroxide, lost chlorine to give methyl 3,4-anhydro- $\alpha$ -D-galactopyranoside (Ia) in good yield. These findings were related to the configurations of the chlorine atom at C<sub>(4)</sub> and the hydroxyl group at C<sub>(3)</sub> in I and II, and it was concluded that a trans configuration was necessary for the elimination of chlorine from C<sub>(4)</sub> to take place.

Since the threeo configuration was retained in I at C<sub>(2)</sub> and C<sub>(3)</sub> during desulphation (1) and the C<sub>(3)</sub> and C<sub>(4)</sub> hydroxyl group and chlorine atom were cis disposed it was concluded that I possessed the galactose configuration and that elimination of hydroxyl at C<sub>(4)</sub> by chlorine had occurred with inversion of configuration.

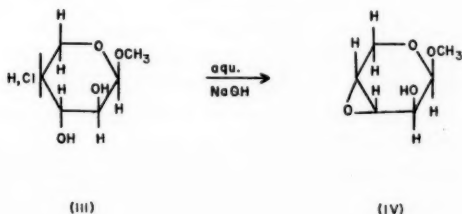
Accordingly I would be methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-galactopyranoside, and the fully substituted compound from which it was obtained by desulphation would be methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-galactopyranoside 2,3-sulphate.

<sup>1</sup>Manuscript received February 29, 1960.

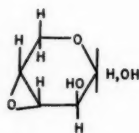
Contribution from the Chemistry Department, Queen's University, Kingston, Ontario.



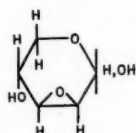
The monochloro monodeoxy pentoside (III) from methyl β-D-arabinopyranoside possessed the chlorine atom at C<sub>(4)</sub> (1). On treatment of III with sodium hydroxide, chlorine was eliminated, presumably with the formation of the anhydro pentoside (IV).



On hydrolysis IV gave two pentoses, D-lyxose and xylose. (The latter was not completely characterized as only a small amount was produced.) The structure of IV was therefore very probably as written, namely, methyl 3,4-anhydro- $\beta$ -D-arabinopyranoside. As shown previously, elimination of chlorine under the influence of sodium hydroxide occurred when the chlorine atom and hydroxyl group involved were trans to one another. Since the configuration of the hydroxyl groups on C<sub>(2)</sub> and C<sub>(3)</sub> did not change on desulphation (1) and C<sub>(3)</sub> and C<sub>(4)</sub> groups were trans, III possessed the L-xylose configuration and was therefore methyl 4-chloro-4-deoxy- $\alpha$ -L-xylopyranoside. The fully substituted compound from which III was obtained by desulphation also possessed the L-xylose configuration and was methyl 4-chloro-4-deoxy- $\alpha$ -L-xylopyranoside 2,3-sulphate. The desulphation of the latter compound was investigated more fully. In addition to methyl 4-chloro-4-deoxy- $\alpha$ -L-xylopyranoside and 4-chloro-4-deoxy-L-xylose, five other compounds were isolated in small amount from the desulphated mixture. They were: two anhydro pentoses, D-lyxose, xylose, and D-arabinose. One anhydro pentose (V) gave on hydrolysis xylose and lyxose, while the other (VI) gave xylose and arabinose which were identified chromatographically because the pentoses were present in too small an amount to be completely characterized in this instance.



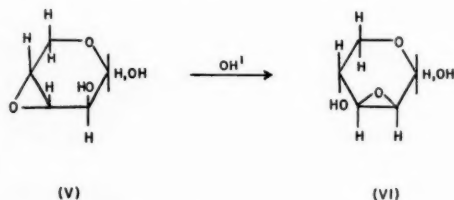
V(3,4-anhydro-D-arabinose)



VI(2,3-anhydro-D-lyxose)

Very probably V and VI gave rise to D-lyxose, xylose, and D-arabinose during the second stage of desulphation (treatment with 2 *N* sulphuric acid). The mechanism of formation of VI is less certain but a possible explanation is outlined below.

An apparently anomalous reaction is proposed in the conversion of methyl 3,4-anhydro- $\beta$ -D-arabinopyranoside 2-sulphate (a postulated reaction intermediate) to methyl 2,3-anhydro- $\beta$ -D-lyxopyranoside by 2 *N* sulphuric acid. Reactions of the type V  $\rightarrow$  VI are



(V)

(VI)

known to occur, under the influence of alkali (4), but not in an acid medium. However, no free ionic sulphate could be detected after the first stage of desulphation (treatment with methanolic ammonia) and the sulphate residue remaining on C<sub>(2)</sub> would presumably prevent migration of the epoxide ring from C<sub>(3)</sub>-C<sub>(4)</sub> to C<sub>(2)</sub>-C<sub>(3)</sub>. Therefore the migration was presumed to occur in the second stage in which the sulphate residue was removed (treatment with 2 *N* sulphuric acid).

The initial reaction in the desulphation, the cleavage of the cyclic sulphate ring with

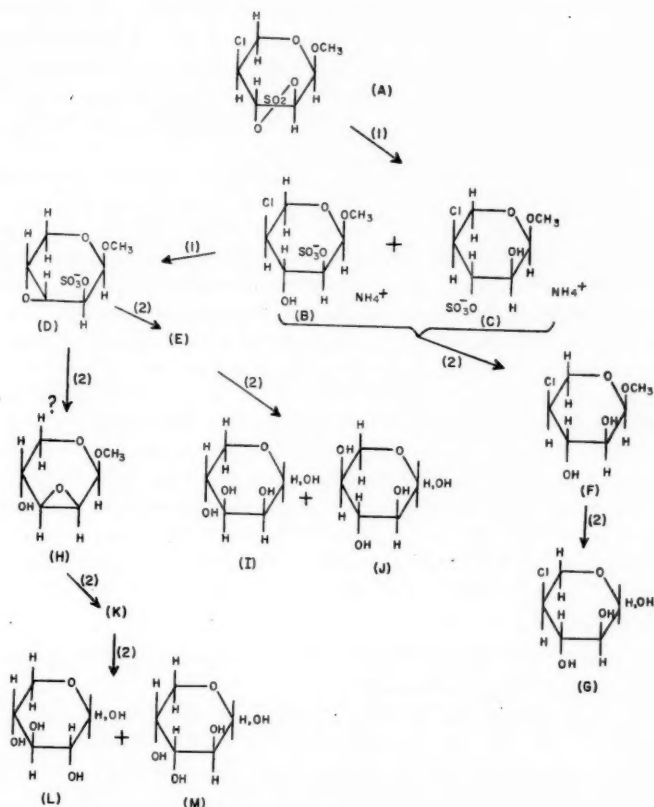


FIG. 1. The desulphation of methyl 4-chloro-4-deoxy- $\alpha$ -L-xyloside 2,3-sulphate (A).

LEGEND: First stage of desulphation (MeOH/NH<sub>3</sub>) (1).

Second stage of desulphation (2 N H<sub>2</sub>SO<sub>4</sub>) (2).

(B) and (C) Ammonium salts of opened sulphate ring. (D) 3,4-Anhydro- $\beta$ -D-arabinose 2-sulphate. (E) 3,4-Anhydro-D-arabinose. (F) Methyl 4-chloro-4-deoxy-L-xylose. (G) 4-Chloro-4-deoxy-L-xylose. (H) 2,3-Anhydro- $\beta$ -D-lyxoside. (I) D-Lyxose. (J) L-Xylose. (K) 2,3-Anhydro-D-lyxose. (L) D-Xylose. (M) D-Arabinose.

ammonia, very probably gave two compounds ((B) and (C) in diagram). The ratio of (B) to (C) was not known, but it was unlikely that a very high proportion of (B) was present, as chlorine would then have been eliminated by the methanolic ammonia due to the trans configuration of the chlorine atom on C<sub>4</sub> and the hydroxyl group on C<sub>3</sub>.

An analogous sequence of reactions leading to the formation of complex mixtures would be expected to occur with all those fully substituted derivatives containing a chlorine atom trans to an adjacent potential secondary hydroxyl group, and this was found to be the case (see above) with methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-glucopyranoside 2,3-sulphate. The corresponding derivative from methyl  $\alpha$ -D-glucopyranoside, possessing the galactose configuration, gave only methyl 4,6-dichloro-4,6-dideoxy- $\alpha$ -D-galactopyranoside (I) and 4,6-dichloro-4,6-dideoxy-D-galactose on desulphation.

## EXPERIMENTAL

Melting points are uncorrected and were determined on a Kofler microheating stage. All evaporations were carried out under reduced pressure. Optical rotations were measured in water at  $21 \pm 3^\circ \text{C}$  unless otherwise stated. Paper chromatograms were run using a descending flow (5) and Whatman No. 1 paper in the following solvent systems:

- (a) butan-1-ol:ethanol:water (3:1:1),
- (b) butan-1-ol:pyridine:water (10:3:3),
- (c) ethyl acetate:acetic acid:formic acid:water (18:3:1:4).

*Reaction of Sulphuryl Chloride with Methyl 4-Chloro-4-deoxy- $\alpha$ -D-glucopyranoside*

The chloro sugar was obtained as a syrup contaminated with a small amount of methyl 3-chloro-3-deoxy- $\alpha$ -D-glucopyranoside, by the method of Buchanan (2). The syrup (0.5 g) gave with sulphuryl chloride a pale yellow syrup (0.388 g) containing sulphur and chlorine. On desulphation first with methanolic ammonia and then with 2 *N* sulphuric acid in the usual manner (1) a complex mixture was obtained (0.180 g) which consisted of seven components  $R_f$  values 0.19, 0.21, 0.40, 0.48, 0.73, 0.78, 0.81, in solvent (a). Alkaline silver nitrate spray (6) was used to detect the sugars. An aqueous solution of the mixture was continuously extracted with chloroform for 24 hours. The chloroform extract on evaporation gave a syrup (43 mg) which crystallized. The syrup contained the three components  $R_f$  0.73,  $R_f$  0.78,  $R_f$  0.81, of which the component  $R_f$  0.78 was the major one. The syrupy crystals were recrystallized twice from chloroform/light petroleum ( $60^\circ$ – $80^\circ \text{C}$ ) to give white needles of melting point  $119$ – $121^\circ \text{C}$  and  $[\alpha]_D^{+21} (c, 1.8)$ . Analysis: Calc.  $\text{C}_7\text{H}_{12}\text{O}_4\text{Cl}_2$ : C, 36.4%; H, 5.2%. Found: C, 37.0%; H, 5.3%.

*Periodate Oxidation of the Methyl Dichloro-dideoxy- $\alpha$ -D-hexoside Prepared from Methyl 4-Chloro-4-deoxy- $\alpha$ -D-glucopyranoside*

The oxidation was carried out at  $25^\circ \text{C}$ , using a small sample (8.5 mg) of the compound in distilled water (25 ml) containing 0.3 *M* sodium metaperiodate (1 ml). The results are shown below and are compared with those of Buchanan (3) for methyl 4-chloro-4-deoxy- $\alpha$ -D-glucopyranoside.

TABLE I

Substance	Time of oxidation (hours)	Consumption of periodate (mole/molecule)	Acid production (mole/molecule)
Methyl dichloro-dideoxy- $\alpha$ -D-hexoside	3.8	0.195	0.00
	10	0.310	
	24.5	0.415	
	167	1.04	
	243	1.07	
Methyl 4-chloro-4-deoxy- $\alpha$ -D-glucopyranoside	20	0.42	Not reported
	40	0.58	
	170	1.03	
	212	1.06	

*Reaction of Sulphuryl Chloride with Methyl  $\alpha$ -D-Galactopyranoside*

Methyl  $\alpha$ -D-galactopyranoside was prepared by the method of Dale and Hudson (7), purified by recrystallization from hot absolute ethanol, and dried *in vacuo* at  $40^\circ \text{C}$ . With sulphuryl chloride, methyl  $\alpha$ -D-galactopyranoside (5 g) gave a brown syrup (3.7 g)



which contained chlorine and sulphur (sodium fusion). The syrup could not be obtained crystalline.

Desulphation of the syrup with methanolic ammonia and 2 *N* sulphuric acid gave a mixture (0.73 g) containing four components of  $R_f$  values 0.12, 0.22, 0.42 (major component), 0.71 (solvent (*a*); alkaline silver nitrate and anisidine hydrochloride (8) sprays). An aqueous solution of the mixture was continuously extracted with chloroform for 24 hours. The chloroform extract on evaporation gave a colorless syrup (0.3 g). On nucleation with the methyl dichloro-dideoxy- $\alpha$ -D-hexoside which had been prepared from methyl 4-chloro-4-deoxy- $\alpha$ -D-glucopyranoside (see above) rapid crystallization occurred.

When recrystallized from chloroform/light petroleum (60°–80° C) the crystals had a melting point of 119–121° C, mixed melting point with the above compound 119–121° C,  $[\alpha]_D^{25} +122^\circ$  (*c*, 1.9) and were therefore identical with that compound. Analysis: Calc. for  $C_7H_{12}O_4Cl_2$ : Cl, 30.7%. Found (Schöniger combustion method (9)): Cl, 30.4%.

#### *The Reaction of Chloro Sugars with Sodium Hydroxide*

##### *The Methyl 4,6-Dichloro-4,6-dideoxy- $\alpha$ -D-hexoside from Methyl $\alpha$ -D-Glucopyranoside (1)*

The hexoside (150 mg) was dissolved in water (25 ml) and phenolphthalein was added. The solution was then titrated with 0.232 *N* sodium hydroxide solution. No sodium hydroxide was neutralized even after 4 hours at 40° C. The solution was deionized with resin and the eluate concentrated to a crystalline mass (151 mg). The crystals had a melting point of 156–158° C and mixed melting point with the starting material, 156–158° C. Analysis: Calc. for  $C_7H_{12}O_4Cl_2$ : Cl, 30.7%. Found: starting material, 31.0%; product, 31.4%.

##### *The Methyl Dichloro-dideoxy- $\alpha$ -D-hexoside from Methyl $\alpha$ -D-Galactopyranoside*

The hexoside (m.p. 119–121° C, 0.875 mg) was dissolved in distilled water (1 ml) and sodium hydroxide solution (1 ml of 0.01 *N*) was added. The solution was allowed to stand for 6 hours at room temperature, then neutralized exactly with 0.01 *N* sulphuric acid, using screened methyl red – methylene blue indicator. To the neutralized solution was added neutralized mercuric oxycyanide solution (5 ml of 2% solution) and the resultant alkaline solution titrated to exact neutrality with 0.01 *N* sulphuric acid. The titer was 0.330 ml, which corresponded to the elimination of 0.88 mole chlorine per molecule of hexoside. The titration mixture was deionized with resin and examined on paper chromatograms. Three components were observed of  $R_f$  values 0.04 (faint), 0.38 (major component), 0.71 (faint co-chromatographing with starting material) (solvent (*a*), alkaline silver nitrate spray).

##### *The Methyl 3-Chloro-3-deoxy- $\alpha$ -D-gulopyranoside (2)*

The gulopyranoside (164 mg) was dissolved in water (25 ml) and titrated with sodium hydroxide (0.232 *N*) as described above. The solution took up 1 equivalent (3.31 ml) of sodium hydroxide over a period of 72 hours at 40° C and was then evaporated to dryness. The residue was extracted three times with 100-ml portions of boiling ether. The combined ether extracts on evaporation gave a syrup (101 mg, 74%) which rapidly crystallized. The crystals had a melting point of 117–118° C undepressed on admixture with an authentic specimen of methyl 3,4-anhydro- $\alpha$ -D-galactopyranoside (m.p. 117.5–118.5° C).

##### *The Methyl 4-Chloro-4-deoxy- $\beta$ -pentoside from Methyl $\beta$ -D-Arabinopyranoside (1)*

The pentoside (67 mg) was dissolved in water (3.0 ml) and sodium hydroxide solution

(0.45 ml of 0.232 *N*) was added. The change in optical rotation was followed at intervals up to 5 hours.

TABLE II

Time of reaction (hours)	$[\alpha]_D$
0	+108°
0.25	+82°
0.50	+73°
1.0	+72°
1.75	+63°
4.0	+61°
5.0	+59°

The slight excess of sodium hydroxide remaining after 8 hours was neutralized with nitric acid, the solution evaporated to dryness, and the residue extracted with ether. The extract on evaporation gave a colorless syrup (47 mg), while the residue gave a positive test for ionic chloride. The syrup gave one main spot,  $R_f$  0.53 (solvent (*a*)), on paper chromatograms. The syrup was heated with 2 *N* sulphuric acid at 100° C for 14 hours, neutralized with barium carbonate, filtered, and deionized with resin. The eluate was concentrated to a colorless syrup (30 mg) which consisted of xylose and lyxose as shown by paper chromatograms, and paper electrophoresis in pH 9.5 borate buffer at 2500 volts for 40 minutes. An attempted separation of the pentoses using phenol saturated with water as the chromatographic solvent (10) with a descending flow on Whatman 3MM paper was unsuccessful. The pentoses were separated by paper electrophoresis under the conditions mentioned above. The lyxose (10 mg)  $[\alpha]_D -18^\circ$  (*c*, 1) was characterized by its rate of movement on chromatograms and as its phenyl osazone, m.p. 158–161° C, unchanged on admixture with authentic D-lyxose (xylose) phenylosazone (11). The xylose could not be satisfactorily characterized due to its small amount (ca. 2 mg).

*The Desulphation of Methyl 4-Chloro-4-deoxy-β-pentoside 2,3-Sulphate (1)*

The desulphated mixture (0.9 g) was separated on a cellulose column using butan-1-ol: water (19:1). Besides methyl 4-chloro-4-deoxy-β-pentoside and 4-chloro-4-deoxy pentose, four other fractions were isolated: Fraction I, a syrup (53 mg) with  $R_f$  0.44 (in solvent (*a*)) was obtained. On hydrolysis with sulphuric acid it gave xylose and lyxose, identified by paper chromatography and paper electrophoresis: Fraction II was a syrup (15 mg) with  $R_f$  0.39 (solvent (*a*)). On hydrolysis it gave xylose and arabinose, identified by paper chromatography and paper electrophoresis. Fraction III was a syrup (78 mg) with  $R_f$  0.24 (solvent (*a*)). This fraction consisted of xylose and lyxose as shown by paper chromatograms and paper electrophoresis. A partial separation was achieved on a column of Dowex 50W sulphuric acid resin (86×2.2 cm, 8% cross-linked with divinyl benzene, 200–400 mesh, barium salt form). The lyxose was obtained pure, and characterized as its *p*-toluene sulphonhydrazone (12), m.p. 152–153° C, which did not depress the melting point of authentic D-lyxose *p*-toluene sulphonhydrazone (141° C). The xylose could not be completely characterized. Fraction IV, syrupy crystals (51 mg),  $R_f$  0.214 (solvent (*a*)), consisted of D-arabinose as shown by paper chromatograms. It was contaminated with some water-insoluble material and had  $[\alpha]_D -74^\circ$  (5 minutes) →  $-66^\circ$  (8 hours) (*c*, 0.4 in methanol). It was characterized as the benzoyl hydrazone, m.p. 190–195° C, undepressed on admixture with authentic D-arabinose benzoyl hydrazone, m.p. 190–195° C (13).

## ACKNOWLEDGMENTS

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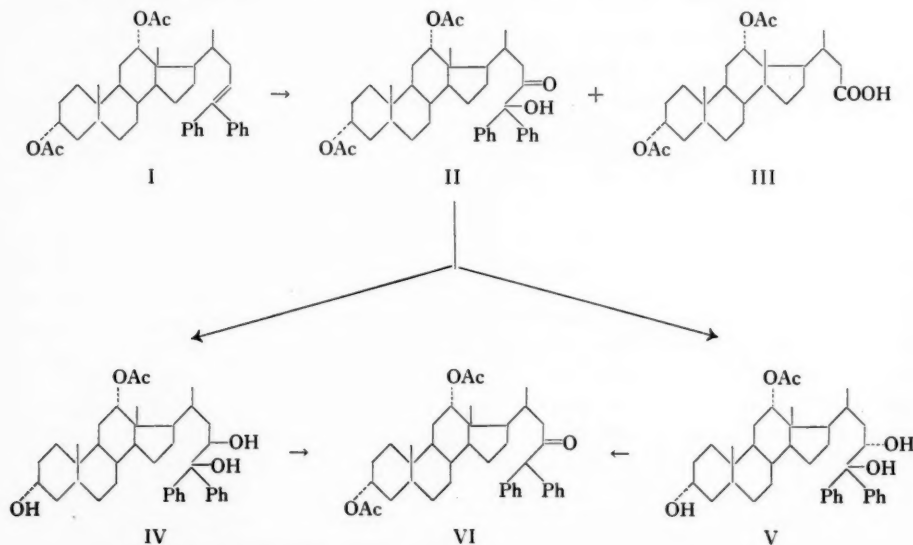
# BILE ACID DERIVATIVES<sup>1</sup>

A. A. AMOS AND P. ZIEGLER

## ABSTRACT

The potassium permanganate oxidation of 3 $\alpha$ ,12 $\alpha$ -diacetox-24,24-diphenyl- $\Delta^{22}$ -cholene yielded a new compound which was identified as 3 $\alpha$ ,12 $\alpha$ -diacetox-23-keto-24-hydroxy-24,24-diphenylcholane. The latter steroid, on reduction with sodium borohydride, produced two isomeric glycols which were subsequently dehydrated to provide the corresponding 23-keto-24,24-diphenyl derivative.

Desoxycholic acid is used extensively as a starting material for the preparation of steroidal hormones. One important phase of this conversion consists of the partial degradation of the bile acid side chain which is attached to C-17 of the steroid nucleus. This degradation can be accomplished by the classical Barbier-Wieland procedure, or preferably by the Miescher-Wettstein (1) scheme. Both methods produce the acetylated diphenylethylene derivative I as an intermediary product. According to the directions of Miescher and Wettstein, I is brominated in the allylic position, then dehydrobrominated to the corresponding diene, which in turn is oxidized to the 20-ketone. It has been found in our laboratories that the dienes thus produced are often contaminated with the ethylene derivative I; this impurity can be detected by its absorption at 252 m $\mu$ . When the crude diene was then treated with potassium permanganate, a useful (2) oxidizing agent for such compounds, the isolation of 3 $\alpha$ ,12 $\alpha$ -diacetoxypregnan-20-one proved to be difficult; in fact, it was found that the yields of 20-ketone increased markedly with increasing purity of diene. This observation indicated that I or its oxidation products interfered with the normal course of the permanganate oxidation of the diene, or with the subsequent isolation of the 20-ketone. It was therefore decided to investigate the products derived from I by this oxidation.



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The oxidation was carried out in refluxing aqueous acetone, containing potassium dihydrogen phosphate as a buffer, which provided the desired neutral pH. The reaction products were then separated to give 30% of acidic material which was identified as nordesoxycholic acid diacetate (III). The neutral fraction, after crystallization, afforded 45% of a compound (II) which in turn was converted to III by oxidation with chromic acid. Compound II failed to react with the Malaprade reagent or with acetic anhydride and pyridine at 20°, and on the basis of this evidence a 23,24-glycol structure was eliminated. The presence of a ketone group in II was indicated clearly by its ultraviolet and infrared absorption, though the compound did not form a 2,4-dinitrophenylhydrazone or an oxime. This result is attributed to steric effects which are known (3) to be operative in similar cases. The ultraviolet spectrum of the ketol II showed bands at 260 m $\mu$  ( $\epsilon$  = 440) and at 297 m $\mu$  ( $\epsilon$  = 360). The absorption at the lower wavelength is undoubtedly due to the two unconjugated phenyl groups (4, 5) in the molecule; the band at the higher wavelength results from the interaction of the ketone function with the phenyl groups. In studies of  $\alpha,\alpha$ -diphenylketones, it has previously been shown (4, 6, 7) that the carbonyl absorption peak in the ultraviolet region is more intense and is shifted towards longer wavelength than that of most ketones. The above data as well as the results of elemental analyses for II and its hydrolysis product provided the evidence for the ketol structure in these compounds.

When the ketol II was reduced with sodium borohydride and the reaction products were hydrolyzed, two isomeric glycols (IV and V) were isolated. Both compounds gave positive Malaprade tests, and the predominant isomer (IV) formed a well-defined acetone; since V was obtained in only small yield, its reactivity towards acetone could not be determined. The two isomers showed the ultraviolet absorption bands at 260 m $\mu$  due to the phenyl groups, but the ketone peak was absent; in the infrared region there appeared the characteristic absorption of associated hydroxyl groups. On treatment with acidic reagents, both glycols yielded 3 $\alpha$ ,12 $\alpha$ -diacetoxo-23-keto-24,24-diphenylcholane (VI). The latter compound again showed the ketone band at 293 m $\mu$ , and in the infrared the hydroxyl peak was absent. These findings, in conjunction with the results of elemental analyses, established the structures for IV, V, and VI.

The oxidation of 3 $\alpha$ ,12 $\alpha$ -diacetoxo-24,24-diphenyl- $\Delta^{23}$ -cholene (I) by chromic acid has been reported (8, 9) to yield 60–70% of the noracid III; ozonization (10) of the diphenylethylene derived from cholic acid afforded the corresponding noracid in lower yield. Invariably, these oxidations produced relatively large amounts of neutral, unidentified fractions which may well contain the related ketols. The good yield of II obtained from the permanganate oxidation is not surprising in view of some recent reports. In the steroid field, this oxidizing agent has been employed to produce ketols from the corresponding  $\Delta^{5,6}$ -unsaturated compounds (11) as well as from  $\Delta^{17,20}$ -analogues (12, 13). The mild permanganate treatment (14) of oleic acid similarly provided high yields (70–75%) of ketohydroxystearic acid.

#### EXPERIMENTAL<sup>2,3</sup>

##### *The Permanganate Oxidation of 3 $\alpha$ ,12 $\alpha$ -Diacetoxo-24,24-diphenyl- $\Delta^{23}$ -cholene (I)*

Compound I (20 g) and potassium dihydrogen phosphate (2 g) were suspended in acetone (195 ml) and water (5 ml). The mixture was stirred and there was then added, in

<sup>2</sup>The microanalyses were kindly performed by Mr. E. Thommen, Basel, Switzerland.

<sup>3</sup>The infrared absorption data were obtained through the courtesy of Dr. G. D. Laubach of Chas. Pfizer & Co., Brooklyn, N. Y.

four equal portions, at intervals of 30 minutes, potassium permanganate (32 g). On addition of each batch of oxidizing agent, vigorous refluxing began and gradually subsided after several minutes. After all the permanganate had been added, the reaction was continued under reflux conditions for an additional  $2\frac{1}{2}$  hours. The excess oxidizing agent was destroyed by charcoal (5 g) and, after 1 hour's stirring, the solids were filtered off. The filtrate was evaporated to dryness, the residue (16 g) was dissolved in ethyl acetate and extracted with 2.5% sodium carbonate solution. After being washed with water, the solvent extract was evaporated, the residual gum was taken up in ether to provide, on cooling, 9.45 g (45%) of II, m.p. 169–171° C. Recrystallization from acetone gave material, m.p. 175–175.5° C, and  $[\alpha]_D^{25} +81.3^\circ$  (*c*, 0.994, dioxane). This compound failed to react with a solution of bromine in carbon tetrachloride, with 2,4-dinitrophenylhydrazine, trichloroacetic acid, the Zimmermann reagent, and was negative in the Malaprade test. Its ultraviolet spectrum showed weak bands at 260  $m\mu$  ( $\epsilon = 440$ ) and at 297  $m\mu$  ( $\epsilon = 360$ ). Analysis: Calculated for  $C_{40}H_{52}O_6$ : C, 76.39; H, 8.34; O, 15.27. Found: C, 76.37, 76.48; H, 8.56, 8.47; O, 15.37, 15.41.

The carbonate extract as well as the water washings from the cake of solids (manganese salts, etc.) were acidified and extracted with ether. The solvent phase was washed, dried, and evaporated; crystallization of the residue from ether–hexane afforded 4.5 g (29%) of crude 3 $\alpha$ ,12 $\alpha$ -diacetoxy-norcholanic acid (III), m.p. 180–190° C. This material was recrystallized from hexane–ether to give a melting point of 203–205° C.

#### 3 $\alpha$ ,12 $\alpha$ -Diacetoxy-norcholanic Acid (III) from II

Compound II (1 g) was suspended in acetic acid (15 ml) and there was then added dropwise, over a period of  $\frac{1}{2}$  hour, a solution of chromic acid (1 g) in acetic acid (24 ml) and water (1 ml). The mixture was kept at 20° C for 2 hours and an equal period of time at 35° C with occasional shaking. The excess oxidizing agent was decomposed by sodium bisulphite; water was added, and the products were extracted with ether. The solvent phase, after having been washed, dried, and evaporated, yielded a residue (1.12 g) which crystallized readily from acetone. The noracid III (472 mg), m.p. 203–205° C, thus obtained, was recrystallized from ether–hexane to give pure III, m.p. 211–213° C.

#### 3 $\alpha$ ,24-Dihydroxy-12 $\alpha$ -acetoxy-23-keto-24,24-diphenylcholanone

The diacetoxy-ketol II (0.5 g) was dissolved by warming in methanol (24 ml) and water (1 ml), containing potassium hydroxide (0.2 g). The solution was kept at room temperature for 66 hours, after which time most of the methanol was removed *in vacuo*. The residue was taken up in ether and dilute mineral acid, the ether phase was washed to neutrality, dried, and evaporated to give a residue (0.46 g) which crystallized from ether–hexane to yield 367 mg of material, m.p. 188–190° C. Two further recrystallizations from ether–hexane provided needles, m.p. 190–191.5° C and  $[\alpha]_D^{24} +68.9^\circ$  (*c*, 0.779, dioxane). Analysis: Calculated for  $C_{38}H_{50}O_6$ : C, 77.78; H, 8.59; O, 13.63. Found: C, 77.83, 77.91; H, 8.75, 8.75; O, 13.63.

#### Sodium Borohydride Reduction of the Ketol II

Compound II (1 g) was partially dissolved in ether (50 ml) and sodium borohydride (0.5 g) was added. The mixture was kept at 20° C for 15 hours, and was subsequently refluxed for  $3\frac{1}{2}$  hours. The excess reducing agent was destroyed by addition of acetic acid, the mixture was diluted with water and extracted exhaustively with ether. The combined solvent extracts were washed, dried, and evaporated to provide a residue (1 g), which



was saponified at room temperature for 15 hours with 2.5% methanolic potassium hydroxide. Dilution with water, extraction with ether, and working up in the usual fashion gave the residue (0.98 g) which crystallized from ether-hexane to provide, in two crops, 451 mg of material; these crystals melted at 127–135° C, the melt resolidified at 145–150° C and finally melted at 215–218° C. Two recrystallizations from ethyl acetate yielded pure IV, m.p. 216.5–219° C and  $[\alpha]_D^{25} +121.2^\circ$  (*c*, 0.366, dioxane). This substance gave a positive Malaprade test; in the ultraviolet region, it exhibited a weak band at 260  $m\mu$  ( $\epsilon = 380$ ). Analysis: Calculated for  $C_{38}H_{52}O_5$ : C, 77.51; H, 8.90; O, 13.59. Found: C, 77.66, 77.55; H, 9.07, 8.99; O, 13.65, 13.74.

The filtrate from IV was reduced in volume and, on refrigeration, three more crops of crystals were isolated. These weighed 295 mg and had a melting point of 177–185° C. Several recrystallizations from ether-hexane provided a small, pure sample of V, m.p. 193–194° C and  $[\alpha]_D^{23} +16.9^\circ$  (*c*, 0.655, dioxane). This compound, on admixture with IV, had a melting point of 178–183° C; V, like IV, gave a positive Malaprade test. Analysis: Calculated for  $C_{38}H_{52}O_5$ : C, 77.51; H, 8.90; O, 13.59. Found: C, 77.78; H, 9.15; O, 13.24.

#### *The Acetonide of IV*

Compound IV (250 mg) was dissolved in dry acetone (20 ml), *p*-toluenesulphonic acid (50 mg) was added, and the solution was kept at 25° C for 16 hours. The solution was neutralized with solid sodium bicarbonate, diluted with water, and extracted with ether. The solvent extract was washed, dried, and evaporated to a white solid (270 mg) which crystallized from ether-hexane to give 220 mg of material, m.p. 227–228° C. Three recrystallizations from the same solvent system yielded the acetonide of IV, m.p. 228–230° C and  $[\alpha]_D^{25} +158.3^\circ$  (*c*, 0.647, dioxane). Analysis: Calculated for  $C_{41}H_{56}O_5$ : C, 78.30; H, 8.98; O, 12.72. Found: C, 78.42, 78.34; H, 9.17, 9.22; O, 12.79, 12.68.

#### *3 $\alpha$ ,12 $\alpha$ -Diacetoxy-23-keto-24,24-diphenylcholate (VI)*

##### *(a) From IV*

Compound IV (120 mg) was refluxed gently for 2 hours with acetic acid (8 ml) and concentrated hydrochloric acid (0.8 ml); an additional 0.8 ml of hydrochloric acid was added then, and refluxing was continued for 2 more hours. The reaction mixture was poured into water, extracted with ether, and the solvent phase worked up in the customary manner. Crystallization of the residue from hexane-ether yielded 70 mg of substance which melted at 127–129° C, partially recrystallized, and finally melted at 155–158° C. Three recrystallizations from hexane-ether provided a pure sample of VI, having a double melting point 133–136° and 167–170° C. When VI is crushed to a very fine powder, it melts at 167–168° C;  $[\alpha]_D^{23} +67.5^\circ$  (*c*, 0.591, dioxane). This compound absorbs in the ultraviolet at 260  $m\mu$  ( $\epsilon = 515$ ) and at 293  $m\mu$  ( $\epsilon = 270$ ). Analysis: Calculated for  $C_{40}H_{52}O_5$ : C, 78.39; H, 8.55; O, 13.05. Found: C, 78.54, 78.77; H, 8.88, 8.53; O, 13.14, 13.05.

##### *(b) From V*

Compound V (80 mg) and *p*-toluenesulphonic acid (300 mg) were refluxed for 3 hours in acetic acid (8 ml). The solution was diluted with water and then extracted with ether; washing, drying, and evaporating the solvent phase provided a residue (86 mg) which crystallized from hexane-ether to give 27 mg of crude VI, m.p. 160–164° C. Recrystallization from ethanol gave pure VI, showing the double melting point, 132–135° C and 165.5–167° C. This material gave no melting point depression on admixture with a sample of VI obtained by dehydration of IV.

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# N-DICHLOROACETYL DERIVATIVES OF SERINE AND THREONINE AND OF THEIR ESTERS AND SODIUM SALTS<sup>1</sup>

I. LEVI, A. E. KOLLER, G. LAFLAMME, AND J. W. R. WEED

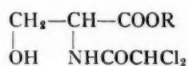
## ABSTRACT

The N-dichloroacetyl derivatives of DL-serine and DL-threonine were prepared by the Schotten-Baumann reaction from the amino acids and dichloroacetyl chloride. Negative ninhydrin tests coupled with elementary analyses indicated that only the amino group was acylated. The ester derivatives of these compounds were prepared either by esterification of the N-dichloroacetyl-DL-amino acid with diazomethane or by the reaction of the amino acid ester with dichloroacetyl chloride in the presence of triethylamine. The sodium salts and the esters were tested for antitumor activity against sarcoma 37 in mice and Walker carcinoma 256 in rats. In both cases regression of the tumors was obtained.

The original studies of Cornman (1) and of Stock, Sugiura, and Rhoads (2) demonstrated that certain antibiotics obtained from the culture filtrates of bacteria and molds inhibited the growth of transplanted tumors in animals. Many other workers have since reported on the antitumor activity of a variety of antibiotic substances (3-16). Two of these antibiotics, azaserine (O-diazoacetyl-L-serine) (15) and DON (6-diazo-5-oxo-L-norleucine) (16), which were isolated from the culture filtrates of two species of *Streptomyces*, and which retarded the growth of sarcoma 180 in the mouse, are diazo amino acids. This is noteworthy because a search for amino acid derivatives which might serve as antagonists in the metabolism of tumor cells, first suggested by Greenberg and Schulman (17), has been going on for many years.

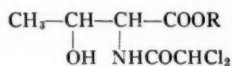
In view of the above, it was reasoned that if some of the common amino acids were modified to contain an essential portion of a natural antibiotic, antimetabolites useful for cancer chemotherapy might result. Since it is generally believed that chloramphenicol is a specific inhibitor of protein synthesis (18), and since the N-dichloroacetyl group is essential for its maximum antibiotic activity (19), it seemed logical to modify the structure of amino acids with the N-dichloroacetyl radical in an attempt to achieve this aim.

A number of N-dichloroacetyl amino acids were therefore prepared and investigated for their pharmacological activities particularly with respect to their antitumor and antibiotic effects. In this paper only serine and its homologue, threonine, are considered because there is a close structural relationship between their N-dichloroacetyl derivatives (Ia and IIa respectively) and chloramphenicol (III), and also because of the unique biological position serine occupies in the metabolism of normal cells (20-27) and of neoplastic cells (28-31).



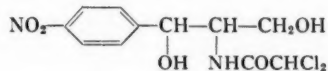
I

Ia, R = H  
Ib, R = Na  
Ic, R = CH<sub>3</sub>  
Id, R = C<sub>2</sub>H<sub>5</sub>



II

IIa, R = H  
IIb, R = Na  
IIc, R = CH<sub>3</sub>  
IId, R = C<sub>2</sub>H<sub>5</sub>



III

DL-Serine was acylated with N-dichloroacetyl chloride in the presence of aqueous sodium hydroxide solution according to the usual Schotten-Baumann procedure. Due to

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Contribution from the Research Laboratories, Charles E. Frosst & Co., Montreal, Que.

the low solubility of its sodium salt (*Ib*) it was possible to recover the major portion of the product in this form from the cold aqueous reaction mixture. However, if the free acid (*Ia*) was desired, the reaction mixture was acidified and worked up in the usual manner.

The free acid (*Ia*) prepared from the sodium salt (*Ib*) by treatment with hydrochloric acid, and the sodium salt prepared from the free acid with sodium hydroxide, were identical in each case with the corresponding products isolated directly from the acylation reaction. Both of these compounds gave a negative ninhydrin test indicating the acylation of the amino group.

The hitherto unreported methyl ester of N-dichloroacetyl-DL-serine (*Ic*) was prepared by two methods. The first consisted in esterifying N-dichloroacetyl-DL-serine with diazomethane, the second in reacting a chloroform solution of DL-serine methyl ester with dichloroacetyl chloride in the presence of triethylamine. The latter method was also employed for the synthesis of the N-dichloroacetyl derivative of DL-serine ethyl ester (*Id*), previously prepared (32) by a modification of this reaction.

DL-Serine methyl ester was prepared as the hydrochloride from DL-serine and hydrogen chloride in anhydrous methanol using a modification of the Fischer esterification technique. Fischer and Suzuki (33) first prepared this ester in 1905 and reported the melting point as 114°. This was confirmed by Mattocks and Hartung (34). Fischer's value was questioned, however, by King (35), who prepared the ester hydrochloride from three different samples of DL-serine and in each case obtained a product which melted at 134°. Chambers and Carpenter (36) confirmed King's melting point as 133–134° and indeed, in our own work, we repeatedly obtained a pure product which melted at 134°.

Similar reactions, applied to DL-threonine, yielded the methyl ester hydrochloride and the hitherto undescribed N-dichloroacetyl-DL-threonine (*IIa*), its sodium salt (*IIb*), and methyl ester (*IIc*). Several attempts to prepare the ethyl ester of N-dichloroacetyl-DL-threonine (*IId*) were unsuccessful, chiefly due to the initial insolubility of DL-threonine ethyl ester (and its hydrochloride) in the solvents such as chloroform, benzene, and ether, normally used in the acylation experiments involving triethylamine. The sodium salt of N-dichloroacetyl-DL-threonine (*IIb*) has a far greater solubility in water than has the sodium salt of N-dichloroacetyl-DL-serine (*Ib*) and therefore could not be isolated directly from the acylation reaction. Although DL-threonine methyl ester hydrochloride can be prepared by the Fischer esterification procedure, the use of thionyl chloride gave a much better yield of product in this case.

The sodium salt of N-dichloroacetyl-DL-serine (*Ib*) has been investigated the most extensively in our laboratories for antitumor activity. It depresses the growth of sarcoma 37 in mice, causing, in some animals, complete regressions of the tumor. The compound is non-toxic to mice in doses up to 4 grams per kilo of body weight. A preliminary report of these results has been published (37).

#### EXPERIMENTAL

The melting points were obtained with a Fisher-Johns apparatus and are uncorrected. Infrared spectra were determined with a Beckman IR-5 spectrophotometer equipped with a sodium chloride prism, using potassium bromide pellets. All melting points and temperature readings are in degrees Centigrade.

##### *Dichloroacylation of DL-Serine*

###### *(a) N-Dichloroacetyl-DL-serine Isolated as Sodium Salt (Ib)*

DL-Serine (36 g, 0.34 mole) was dissolved in 4 N sodium hydroxide solution (85.6 ml,

0.34 mole) in a 1 liter, four-necked, round-bottomed flask fitted with a thermometer, motor-driven stirrer, and two dropping funnels. The clear colorless solution of the sodium salt of DL-serine was cooled in an ice-salt mixture to  $-5^{\circ}$ . Dichloroacetyl chloride (63.2 g, 0.42 mole) and 4 N sodium hydroxide solution (107 ml, 0.42 mole) were then added dropwise and simultaneously from the two dropping funnels to the stirred, cooled solution at such a rate that the reaction mixture remained on the basic side throughout the additions and the temperature of the reaction mixture remained at  $0^{\circ} \pm 4^{\circ}$ .\* During these additions, which required about one hour, the product settled out as a fine white crystalline precipitate. When the additions were completed the reaction mixture was stirred in the cold for an additional 30 minutes. The product, 38.6 g (47.3% yield), was removed by filtration, washed with a little ice-cold water, and dried at  $50^{\circ}$  in a vacuum oven, m.p.  $172-176^{\circ}$ . After recrystallization from water, the sodium salt of N-dichloroacetyl-DL-serine melted at  $178-179^{\circ}$ . It has a solubility in water of 11% at  $27^{\circ}$ , is slightly soluble in cold ethanol, and insoluble in most other organic solvents. Heating at  $105^{\circ}$  for 1 hour did not change its physical appearance, melting point, or infrared absorption curve. When recrystallized from water it retains approximately 15% by weight of the water, which is not substantially removed by air-drying. The anhydrous product is obtained by drying under a pressure of less than 1 mm for a period of 6 hours at  $60^{\circ}$ . Anal. Calc. for  $C_5H_6Cl_2NO_4Na$ : C, 25.23; H, 2.54; N, 5.89. Found: C, 25.09; H, 2.42; N, 5.75.

The filtrate from the crude product of (a) was acidified and worked up as described below in (b) to yield 4.0 g (5.4%) of N-dichloroacetyl-DL-serine (Ia), m.p.  $118-119^{\circ}$ .

*(b) N-Dichloroacetyl-DL-serine Isolated as the Acid (Ia)*

The acylation of DL-serine (21 g, 0.2 mole) was carried out as for the sodium salt derivative described above, which in this case was not isolated. Instead, the total reaction mixture was acidified with dilute hydrochloric acid (7.3 g concentrated hydrochloric acid in 192 ml water) and the clear, colorless solution was concentrated to dryness under vacuum, using a water bath at  $60$  to  $70^{\circ}$ . The residue, which consisted of pale yellow viscous syrup mixed with crystalline sodium chloride, was extracted with hot ethyl acetate ( $4 \times 100$  ml). The combined extracts were dried over anhydrous magnesium sulphate, filtered, and the filtrate again evaporated to dryness as above. The resulting residual light yellow clear oil was shaken with petroleum ether ( $30-60^{\circ}$ ) ( $2 \times 50$  ml) to remove any dichloroacetic acid present, and crystallized from ethyl acetate - petroleum ether ( $30-60^{\circ}$ ) to give 16.4 g (38%) Ia, m.p.  $116-118^{\circ}$ . (Other experiments gave yields up to 55.9%.)

An analytical sample recrystallized from ethyl acetate consisted of a fine crystalline powder which melted at  $119-121^{\circ}$ . It is soluble in ethanol, acetone, diethyl ether, dioxane, and ethyl acetate, is insoluble in ethylene dichloride, N-hexane, benzene, and petroleum ether. It has a solubility in water of 41% by weight at  $27^{\circ}$ . Anal. Calc. for  $C_5H_7Cl_2NO_4$ : C, 27.80; H, 3.26; N, 6.48. Found: C, 27.69; H, 3.22; N, 6.60.

This product (2 g) was dissolved in 10% sodium hydroxide solution (3.6 ml) and the solution evaporated to dryness. The partially solidified colorless residue was recrystallized from ethanol yielding crystals of Ib, m.p.  $176-178^{\circ}$ , the infrared absorption curve of which was identical with that of Ib described above in (a).

*N-Dichloroacetyl-DL-serine from the Sodium Salt*

The sodium salt of N-dichloroacetyl-DL-serine (Ib) (5.0 g) was dissolved in dilute

\*Subsequent experiments indicated that this low temperature range is not critical, since the same yield of product was obtained when the acylation was carried out between  $15^{\circ}$  and  $20^{\circ}$ .



hydrochloric acid solution (25 ml water containing 2.1 ml concentrated hydrochloric acid). The clear solution was evaporated to dryness under vacuum at 50–60°. The residue was extracted with hot ethyl acetate (4×15 ml). The combined extracts were dried over anhydrous magnesium sulphate, filtered, and concentrated to yield an oil, which solidified to a mass of white crystals (3.3 g). Recrystallization from ethyl acetate – petroleum ether yielded N-dichloroacetyl-DL-serine (Ia), m.p. 118–119°, the infrared absorption curve of which was identical with that of Ia described above. The melting point of a mixture of the two was not depressed.

*DL-Serine Methyl Ester Hydrochloride*

A rapid stream of dry hydrogen chloride gas was passed into a suspension of 1 mole of serine (105 g) in anhydrous methanol (500 ml) until the serine dissolved and the clear solution reached its boiling point. The alcohol was then distilled off under reduced pressure. The oily residue was redissolved in fresh anhydrous methanol (500 ml), the solution cooled in an ice bath, and again saturated with a stream of hydrogen chloride gas, during a 1-hour period. The product resulting from the removal of the methanol after this second treatment with hydrogen chloride gas was washed with anhydrous ether (3×50 ml) and dissolved in anhydrous methanol (100 ml) to which a few milliliters of anhydrous ether was added. The ester hydrochloride began to crystallize almost at once. Weight 135 g (87% yield), m.p. 134° (35, 36). Anal. Calc. for  $C_4H_{10}ClNO_3$ : C, 30.87; H, 6.47; N, 9.00. Found: C, 30.67; H, 6.30; N, 9.01.

*DL-Serine Ethyl Ester Hydrochloride*

This compound was prepared from serine (105 g, 1.0 mole) and anhydrous ethanol according to the procedure described above for the methyl ester hydrochloride. The product (144.1 g, 85% yield) was obtained as white crystals which, after recrystallization from ethanol–ether, melted at 98°. The melting point for this ester hydrochloride has been reported as 94–97° (38) and 100–102° (39). Anal. Calc. for  $C_5H_{11}ClNO_3$ : N, 8.26. Found: N, 8.31.

*N-Dichloroacetyl-DL-serine Methyl Ester (Ic)*

*(a) By Esterification of N-Dichloroacetyl-DL-serine with Diazomethane*

N-Dichloroacetyl-DL-serine (Ia) (12.0 g) was covered with ether (100 ml) in a 1-liter round-bottomed flask. An ether solution containing diazomethane (approximately 4.7 to 5.0 g) prepared from N-nitroso-N-methyl urea (17.7 g) was added cautiously and with stirring to this partially dissolved mixture. When the evolution of nitrogen subsided the clear yellow solution was allowed to stand in a fume hood overnight. It was then filtered from a small amount of extraneous material and glacial acetic acid (2 ml) was added to destroy residual diazomethane. The residue obtained on removal of the ether yielded long white needles of Ic (7.2 g, 56.7%), and an additional 3.2 g (25.2%) of crystalline product was recovered from the mother liquors. An analytical sample was recrystallized from ether – petroleum ether and dried over  $P_2O_5$  at 60° for 8 hours, m.p. 82–83.5°. It is soluble in water (20% at 27°) and in most common organic solvents. Anal. Calc. for  $C_6H_9Cl_2NO_4$ : C, 31.32; H, 3.94; N, 6.09. Found: C, 31.36; H, 3.85; N, 6.28. The infrared absorption curve of this product was identical with that of the same product synthesized by route (b) below.

*(b) By N-Dichloroacylation of DL-Serine Methyl Ester*

Triethylamine (101 g, 1.0 mole) was added to DL-serine methyl ester hydrochloride (155.6 g, 1.0 mole) suspended in chloroform (1000 ml). The liberated ester base and the



triethylamine hydrochloride dissolved in the chloroform. The clear solution was cooled in a salt-ice bath to  $-5^{\circ}$ . Dichloroacetyl chloride (147.5 g, 1.0 mole) and a second portion of triethylamine (101.0 g, 1.0 mole) were then added simultaneously and dropwise over a period of  $1\frac{1}{2}$  hours so that the temperature in the reaction flask did not rise above  $10^{\circ}$ . When the additions were completed the solution was stirred at room temperature for an additional half hour. It was then filtered from some extraneous material and the chloroform removed with vacuum from a water bath at  $40-50^{\circ}$ . The residual oily solid was extracted with boiling anhydrous ether ( $4 \times 100$  ml) whereby the product was separated from ether-insoluble triethylamine hydrochloride. The hot ether solution was filtered and on cooling deposited a voluminous mass of white feathery crystals (132.5 g, 57% yield), m.p.  $82-83^{\circ}$ . Anal. Calc. for  $C_6H_9Cl_2NO_4$ : C, 31.32; H, 3.94; N, 6.09. Found: C, 31.34; H, 3.98; N, 6.37.

*N-Dichloroacetyl-DL-serine Ethyl Ester (Id)*

This compound was prepared from DL-serine ethyl ester hydrochloride (84.8 g, 0.5 mole), triethylamine (101.0 g, 1.0 mole), and dichloroacetyl chloride (73.7 g, 0.5 mole) in chloroform solution following the procedure described above for the preparation of Ic. The colorless compound (65.7 g, 53% theory) was recrystallized from diethyl ether, m.p.  $75-76^{\circ}$  (literature value for m.p.  $76^{\circ}$ ) (32). Anal. Calc. for  $C_7H_{11}Cl_2NO_4$ : C, 34.44; H, 4.54; N, 5.73. Found: C, 34.41; H, 4.38; N, 5.75.

*N-Dichloroacetyl-DL-threonine (IIa)*

This compound was prepared from DL-threonine (238 g, 2.0 mole) and dichloroacetyl chloride (368.8 g, 2.5 mole) in the presence of 6 *N* sodium hydroxide solution (750 ml) according to the above described procedure for serine. Yield, 218.9 g (47%), colorless crystals, m.p.  $138-140^{\circ}$ . An analytical sample recrystallized from ethyl acetate melted at  $140-141^{\circ}$ . Anal. Calc. for  $C_6H_9Cl_2NO_4$ : C, 31.32; H, 3.94; N, 6.08. Found: C, 31.14; H, 3.99; N, 6.17.

*Sodium Salt of N-Dichloroacetyl-DL-threonine (IIb)*

N-Dichloroacetyl-DL-threonine was treated with sodium hydroxide according to the procedure described above for the preparation of Ib. The crystalline product, after three recrystallizations from methanol-diethyl ether melted at  $176-178^{\circ}$ . The sodium salt was very soluble in water, soluble in ethanol, and insoluble in the common organic solvents. Anal. Calc. for  $C_6H_8Cl_2NO_4Na$ : C, 28.59; H, 3.20; N, 5.56. Found: C, 28.60; H, 3.00; N, 5.56.

*DL-Threonine Methyl Ester Hydrochloride*

Thionyl chloride (14.9 ml, 0.2 mole) was added carefully to methanol (100 ml) and maintained at  $-10^{\circ}$  by cooling in a salt-ice bath. To this solution was then added 23.8 g (0.2 mole) of DL-threonine and allowed to stand 2 hours at room temperature and then refluxed for 20 minutes. The solution was concentrated to dryness under reduced pressure and the residual oil crystallized from anhydrous methanol-diethyl ether. The product was obtained as colorless needles. Weight 19.9 g (58.7%), m.p.  $124-125^{\circ}$  (lit. m.p.  $125^{\circ}$ ) (40). A second crop, 5.3 g (15.6%), of less pure material (m.p.  $118-120^{\circ}$ ) was recovered from the filtrate. An analytical sample was obtained by recrystallization from methanol-ethyl ether, m.p.  $125^{\circ}$ . Anal. Calc. for  $C_5H_{12}ClNO_3$ : C, 35.40; H, 7.13; N, 8.26. Found: C, 35.18; H, 6.98; N, 8.26.

*N-Dichloroacetyl-DL-threonine Methyl Ester (IIc)*

DL-Threonine methyl ester hydrochloride (8.48 g, 0.05 mole), triethylamine (10.1 g,

0.10 mole), and dichloroacetyl chloride (7.37 g, 0.05 mole) were reacted in 75 ml chloroform following the procedure described above for 1c. The white crystalline compound (10.7 g, 87% yield) melted at 105–106°. An analytical sample was prepared by recrystallization from diethyl ether, m.p. 106°. In contrast to the high solubility in water of the corresponding serine derivative (1c) this compound had a solubility of 5.9% at 27°. Anal. Calc. for  $C_7H_{11}Cl_2NO_4$ : C, 34.44; H, 4.05; N, 5.74. Found: C, 34.31; H, 4.27; N, 5.76.

#### ACKNOWLEDGMENT

The authors wish to thank Mrs. G. Shimizu for the analyses.

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# ANODIC OXIDE FILMS ON NIOBIUM: THICKNESS, DIELECTRIC CONSTANT, DISPERSION, REFLECTION MINIMA, FORMATION FIELD STRENGTH, AND SURFACE AREA<sup>1</sup>

L. YOUNG

## ABSTRACT

The wavelengths of minimum specular reflectivity (at 11° incidence) due to interference were determined using a spectrophotometer for a series of films formed on chemically polished niobium. With a value of the refractive index  $n = 2.46 \pm 1\%$  at 4358 Å wavelength by the Abelès method (reported elsewhere), the spectrophotometric data give the refractive index as a function of the wavelength  $\lambda$ ,  $n = 2.26 + 0.398/(\lambda/10^3 \text{ Å} - 2.56)^{1/2}$ . To analyze the spectrophotometric results, an auxiliary measure of thickness was required (though, with the chart given below, the thickness of a film may be determined directly from spectrophotometric measurements alone). A combination of measurements of the a-c. capacity and of the charge required to form the films gives a suitable measure of thickness (in terms of  $\rho/\epsilon$ , where  $\epsilon$  = dielectric constant and  $\rho$  = density) which is not dependent on a knowledge of the true surface area. The spectrophotometric data provide a calibration of this measure of thickness and thus give  $\epsilon/\rho$ . With  $\rho = 4.36 \text{ g cm}^{-3}$  (reported for the bulk amorphous oxide) this gives  $\epsilon$  about 41 (compared with about 27.6 for  $\text{Ta}_2\text{O}_5$ ). The effective surface area of the chemically polished metal was then found to be about 7% greater than the apparent area. At the ionic current density used to form the films ( $10 \text{ ma cm}^{-2}$ ), the field strength in the oxide was estimated as  $4.96 \times 10^6 \text{ v cm}^{-1}$  within a few per cent uncertainty. Because the field to produce a given ionic current is lower than with  $\text{Ta}_2\text{O}_5$  films, the capacity of films formed to a given voltage at a given current density and temperature is not so much greater for niobium than for tantalum as the dielectric constants might lead one to expect. It is suggested that there may be a correlation between dielectric constant and ionic conductivity. The  $\text{Nb}_2\text{O}_5$  films recrystallize like  $\text{Ta}_2\text{O}_5$  films under an applied field but more readily, at least with the purity of metal now available.

## INTRODUCTION

As might be expected from their close chemical similarity, niobium and tantalum behave very similarly when anodically polarized. The present investigation of some of the properties of the film material followed the same method as was applied recently to tantalum (1). The aim was to obtain further data towards the comparative study of the various metals (Al, Nb, Ta, Ti, Zr, W, etc.) which show similar anodic film forming properties. Niobium is of particular interest because of its possible future use as an electrolytic capacitor anode. The kinetics of formation and some other topics have been discussed elsewhere (2, 3, 4).

## EXPERIMENTAL METHODS

The electrodes ( $2 \times 0.5 \text{ cm}$  with a tab) were cut (using a die to obtain a reproducible size) from Fansteel Metallurgical Corporation 0.005-in. sheet of greater than 99.9% purity. They were stopped off and chemically polished as previously described (2). To obtain uniformity in the surface finish they were prepared in batches. After being stored dry, they were dipped in a dichromate-sulphuric acid cleaning mixture before use.

The solution was 0.2  $N$   $\text{H}_2\text{SO}_4$  in demineralized water. The cell was immersed in a water thermostat at 25.8° C. The oxide films were formed at a constant current density of about  $10 \text{ ma cm}^{-2}$ . This high current density was chosen to obtain the maximum current efficiency. An electronic, automatic control device was used which records the times to traverse intervals of potential (about 4 seconds for 10 volts at the current density used) and terminates formation at a preset potential with respect to a reference electrode. At

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Contribution from the British Columbia Research Council, University of British Columbia, Vancouver 8, British Columbia.

this current density, it is necessary to circulate the solution rapidly to eliminate heating effects (5).

A Cary double-beam recording spectrophotometer was used to locate the minima in the specular reflectivity at an angle of incidence of  $11^\circ$ . A simple device was specially made to hold the specimens and two front aluminized mirrors which reflected the light beam on to the specimens and back into its original path. A specimen which had been chemically polished but not anodized was used in the reference beam.

The capacity measurements were made at 1 kc/sec with a small a-c. signal.

## RESULTS

The specimens were first formed to 10 v and the capacity was measured. The formation was then continued to the final potential. A procedure of this sort is necessary because of the pre-existing film. The charge to form to 10 v depends on the thickness of the film already present—and its measurement could be used to determine the thickness of this film and might prove a better method than anodic polarization measurements at low current densities (6, 7) where leakage current tends to interfere—but the charge to form from 10 to (say) 100 v can reasonably be assumed to be independent of the thickness of the pre-existing film. Similar considerations apply to the reciprocal capacity.

The increase in the reciprocal of the series equivalent capacity  $C$  which occurs when the thickness of the film is increased by an amount  $x$  is assumed to be given by

$$[1] \quad \Delta(1/C) = 4\pi x/\epsilon A$$

where  $\epsilon$  = dielectric constant and  $A$  = effective area. The amount of charge which must flow through the film to produce the increment of thickness is assumed to be

$$[2] \quad Q = Ax\rho 10F/M$$

where  $\rho$  = density,  $F$  = the Faraday, and  $M$  = molecular weight of  $\text{Nb}_2\text{O}_5$ . It is assumed that the film is  $\text{Nb}_2\text{O}_5$  and that it does not contain appreciable amounts of water or anions. From [1] and [2]

$$[3] \quad \{Q\Delta(1/C)\}^{1/2} = x(4\pi\rho 10F/\epsilon M)^{1/2}.$$

The expression on the left-hand side gives a measure of thickness (in terms of the ratio,  $\rho/\epsilon$ ) which is independent of the area of the surface. The above expressions are not exact if  $A$  changes with thickness but [3] is a good approximation if  $A$  only changes slightly.

The wavelengths of the minima in the specular reflectivity are plotted against the above measure of thickness in Fig. 1. Since the frequency of "leaky" and otherwise abnormal specimens is of interest, the results obtained from all the specimens are plotted though only those for films of less than about 2200 Å thickness have been used in the calculations. Two types of non-ideal behavior occurred as the thickness increased: (a) decreased  $dV/dt$  ( $V$  = potential,  $t$  = time) due to leakage paths developing in the oxide giving oxygen evolution and (b) steadily increasing  $dV/dt$ , previously associated (with tantalum) with surface roughness (8, 9). At lower current densities, recrystallization has time to occur. Less pure niobium showed much worse behavior, and was also less easy to polish chemically to a satisfactory finish.

The minima\* in the reflectivity are caused by destructive interference. This occurs when

$$[4] \quad 2n \cos \theta (D+X) = \{(2r-1)/2\}\lambda$$

\*The maxima could be used but less satisfactorily since they are less sharp.

where  $D$  = film thickness,  $n$  = refractive index;  $\theta$  = angle of refraction;  $X$  = a constant at a given wavelength which allows for the difference between the phase changes during reflection at the oxide/air and metal/oxide interfaces respectively;  $r = 1, 2, 3 \dots$ ; and  $\lambda$  = wavelength. Consequently, the vertical separation between the curves in Fig. 1 corresponds to an increase in thickness ( $\lambda/2n \cos \theta$ ).

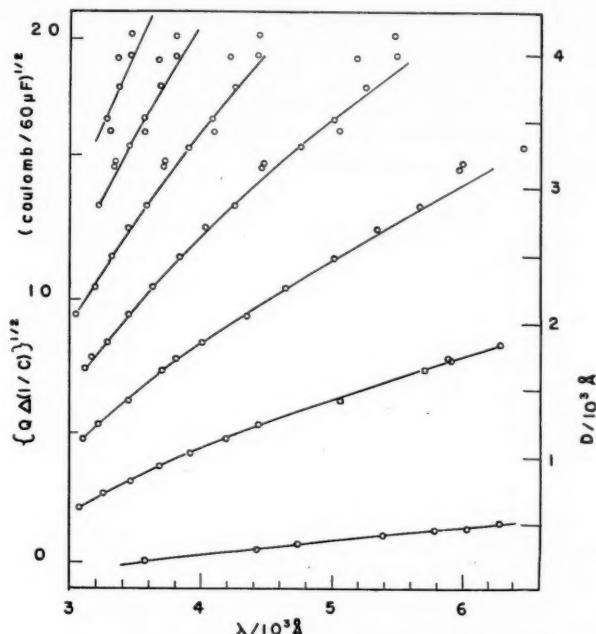


FIG. 1. Wavelengths at which destructive interference occurred plotted against  $\{Q\Delta(1/C)\}^{1/2}$ . A scale in angstrom units is given at the right.

A value of  $n$  at one wavelength is required to obtain a calibration of the thickness. Durbin, Wagner, and Harman (10) have recently determined  $n$  for the two axes of the high temperature crystalline modification of  $\text{Nb}_2\text{O}_5$  as 2.27 and 2.31 in sodium light. Holtzberg, Reisman, Berry, and Berkenblit (11) have determined the densities at 25° C of some of the various forms. These are: amorphous, 4.36 g cm<sup>-3</sup>;  $\gamma$ , 5.17 g cm<sup>-3</sup>; and  $\alpha$ , 4.55 g cm<sup>-3</sup>. Assuming that  $(n-1)/\rho$  = constant, we obtain  $n = 2.24$  for the amorphous oxide.

The Becke immersion method (1) was not applied to the films because it was found to be difficult to strip sufficient oxide. Orme and Young (unpublished) have used the Brewster angle method of Abelès (12). They found that the reflectivity of the oxide coated metal for light of wavelength 4358 Å polarized in the plane of incidence was independent of the thickness of oxide at an angle of incidence 67° 51'. This shows that the index of the outer layers of oxide is constant at a value  $\tan 67^\circ 51' = 2.46$ . The uncertainty is about  $\pm 1\%$ . With the present evidence that capacity, Faraday's laws, and spectrophotometric data are consistent with a uniform film (apart from the pre-existing film), the above index is assumed to be that of the whole film.

With this value for  $n$  at 4358 Å, and with the value of  $\rho/n^2\epsilon$  from the data of Fig. 1,

we obtain  $\epsilon$  about 41.4. The dependence on assumed constants may be expressed by writing  $\epsilon = 41.4 (\rho/4.36 \text{ g cm}^{-3}) \{2.46/n(4358 \text{ \AA})\}^2$ . Apart from the uncertainty due to the uncertainty in  $\rho$  and  $n$ , this value is believed to be accurate to within 2 or 3% for the experimental conditions stated. With the refractive index known at one wavelength, the values of the thickness increments  $\lambda/2n \cos \theta$  at other wavelengths give the refractive index at these wavelengths (Fig. 2). The smooth curve is the Hartmann equation,  $n = 2.26 + 0.398(\lambda/10^3 \text{ \AA} - 2.56)^{-1.2}$ . The value of  $\lambda_0$  in  $n = a + b(\lambda - \lambda_0)^{-1.2}$  is greater than the value for  $\text{Ta}_2\text{O}_5$  films (1), and although the Hartmann equation is empirical, this difference does in fact correspond to a greater long wavelength limit of the intrinsic absorption. This had the effect that the measurements could only be taken to about 3000 Å. With tantalum the limit was about 2700 Å. As with  $\text{Ta}_2\text{O}_5$  films, the minima became very flat beyond 6000 Å wavelength.

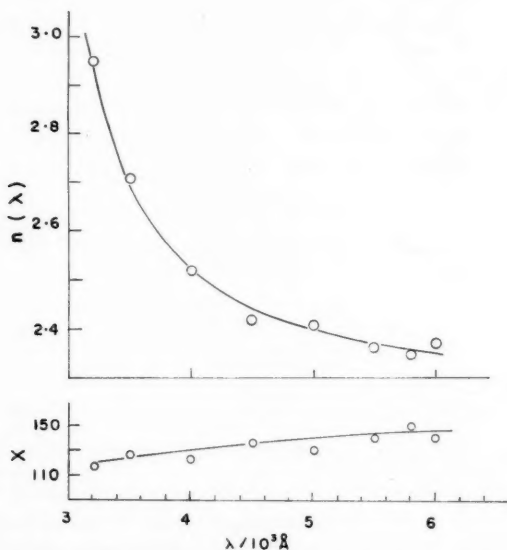


FIG. 2. Refractive index of films, and  $X$  (equation 4) as function of wavelength.

The ratio of increments of potential to increments of thickness is one measure of the field strength in the oxide. (Strictly, the field strength, like absolute metal/solution potential differences, is not an experimental observable, but it can be approximated if suitable assumptions are made.) The values obtained are shown in Fig. 3 as a function of voltage and thickness. The mean below 120 volts is  $E = 4.96 \times 10^6 \text{ v cm}^{-1}$ , with an uncertainty of 1% due to the uncertainty in  $n$ , and a further 2 or 3% due to other sources of error.

Estimates of the field are also given in Fig. 3 with the thickness obtained from the charge passed using Faraday's laws with the "apparent" area. These estimates differ systematically from the above values because the effective area is greater than the apparent area.

With the dielectric constant now determined, the combination of capacity and Faraday's



law data give an estimate of the ratio of the effective to the apparent area. From [1] and [2]

$$A/a = (1/a)(M4\pi/10\rho F\epsilon)^{1/2} \{Q/\Delta(1/C)\}^{1/2}.$$

The values obtained are plotted in Fig. 3. They indicate a slight decrease in area with increasing thickness of oxide. This would not be unexpected since it would occur if there were surface irregularities on the scale of the thickness of the oxide film, but it could also be due to a deviation from the ideal behavior assumed in [1] and [2].

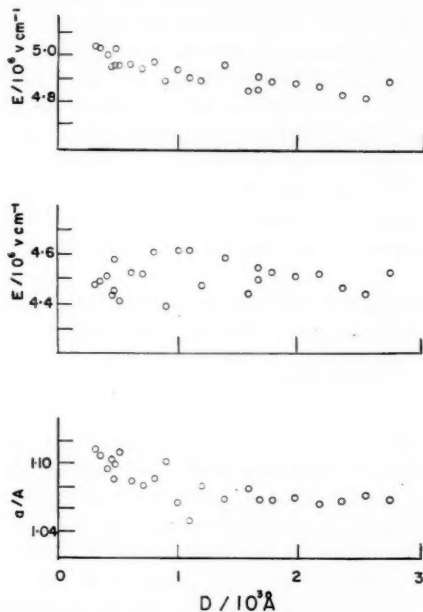


FIG. 3. (Top) Field strength  $(V/\{Q\Delta(1/C)\}^{1/2})$ . One point per specimen.  
 (Middle) Apparent field strength using thickness calculated from charge passed assuming  $a = A$ , and  $\rho = 4.36 \text{ g cm}^{-3}$ .  
 (Bottom)  $A/a$  = ratio of effective to apparent area.

The above procedures establish the thickness of the films only with reference to an arbitrary zero, namely the thickness of films formed to 10 volts (sat. cal.) under the conditions stated. The optical method does not give an absolute measure of thickness because the optical constants of the metal are not known with sufficient accuracy. Instead, having shown that  $\Delta V/\Delta D$  is constant (Fig. 3), we assume that, if  $V - V_0$  is the overpotential for the production of oxide,  $(V - V_0)/D = \Delta V/\Delta D$ . This gives the zero of the scale of thickness to the right of Fig. 1 and the values of  $X$  (equation 4) shown in Fig. 2.

The films recrystallize under the influence of an applied field in very much the same manner as do those on tantalum (Vermilyea (13)). However, with our samples of metal, the crystalline nuclei appeared much more quickly than with tantalum. In contrast with tantalum, the kinetics were not very sensitive to the surface preparation (chemically polished, etched in HF, mechanically polished) though the shape of the crystalline areas

varied (e.g. mechanically polished surfaces gave epicycloid-shaped areas). Sectors like those which are seen with crossed nicols in  $\text{Ta}_2\text{O}_5$  crystalline areas were not apparent.

#### DISCUSSION

The thickness of a given film can be obtained within a few per cent by the use of Fig. 1 in conjunction with a simple spectrophotometric measurement. The curves in Fig. 1 for films thicker than about 2000 Å are based on the results for the thinner films (using [4]).

In an earlier paper (3), the thickness was calculated from the charge passed (using [2]) taking  $a = A$  and assuming  $\rho = 5 \text{ cm}^{-3}$  (which was about in the middle of the range of the values of  $\rho$  reported at that time). The corrections for conversion to  $\rho = 4.36 \text{ g cm}^{-3}$ , and  $A = (1.07a)$  cancel. The experimental results are, therefore, in good agreement (the ratio  $A/a$  may have been slightly different). In the earlier work, the field strength was determined only at lower current densities but extrapolation gives a value of about  $4.4 \times 10^6 \text{ v cm}^{-1}$ , which is again in satisfactory agreement with present values calculated in the same way from [2] with  $a = A$  (Fig. 3).

The large difference between the dielectric constants for  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  (27.6) is notable. It could be due either to an extra contribution to  $(\epsilon - n^2)$  of the infrared lattice vibrations in  $\text{Nb}_2\text{O}_5$ ,\* or to a larger contribution from ionic relaxation processes associated with interstitial ions.

The ratio of the a-c. capacities per unit area of niobium and tantalum electrodes formed to the same potential at the same current density and temperature is given by

$$(E_{\text{Nb}_2\text{O}_5} \epsilon_{\text{Nb}_2\text{O}_5}) / (E_{\text{Ta}_2\text{O}_5} \epsilon_{\text{Ta}_2\text{O}_5})$$

where  $E$  = field strength in the oxide. At  $10 \text{ ma cm}^{-2}$  this ratio is between 1.1 and 1.2. The lower field strength required in  $\text{Nb}_2\text{O}_5$  to give a particular ionic current thus means that the high dielectric constant does not give much advantage in using niobium in place of tantalum in electrolytic capacitors, the chief advantages to be obtained being the more plentiful reserves of the metal and its lower density.

The above results are applicable only to films formed in dilute solution.

The fact that with  $\text{Al}_2\text{O}_3$  films the dielectric constant is again lower (about 10), and the fields higher, suggests that there is a correlation between the dielectric properties of the oxide and its ionic conductivity.

#### ACKNOWLEDGMENTS

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\* $\epsilon - n^2 = 4[(n^2 + 2)/3]^2 (e^2 N / m \omega_i^2)$  where  $e$  = effective charge on ions,  $N$  = number of unit cells per unit volume,  $m$  = reduced mass of ions,  $\omega_i$  = traverse vibration frequency (14). If  $\omega_i$  were assumed to be about the same, the observed difference could be ascribed to  $m$ .

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# ALIPHATIC CHEMISTRY OF FLUORENE

## PART VI. 3,4-BENZOFLUORENE-9-SPIRO-CYCLOHEXANE<sup>1</sup>

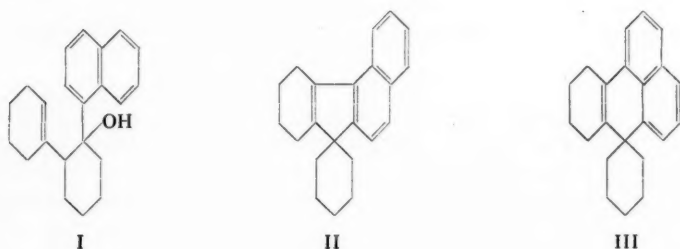
P. M. G. BAVIN<sup>2</sup>

### ABSTRACT

The quinoxaline (VI) has been prepared from 3,4-benzofluorene, establishing the structure of the cyclization product of I as 3,4-benzo-5,6,7,8-tetrahydrofluorene-9-spiro-cyclohexane. 3,4-Benzo-9,9-dimethylfluorene has been prepared and oxidized to the quinone (VIII) which formed the quinoxaline (IX), structurally related to VI.

1,2:7,8-Dibenzo-9-methylfluorene has been synthesized from 1,2:7,8-dibenzofluorenone which, contrary to an earlier report (13), forms an oxime.

Cyclization of the tertiary alcohol (I)\* by aluminum chloride was shown to give a hydrocarbon A, for which two structures have been proposed (II (1, 2), III (3)). Dehydrogenation of A gave a new hydrocarbon B, by loss of four atoms of hydrogen. Oxidation of B gave a crimson quinone which, contrary to an earlier report (3), has now been shown to condense with *o*-phenylenediamine with formation of a quinoxaline. The structures of the hydrocarbons A and B have been established by preparing the quinoxaline from 3,4-benzofluorene.



The reaction between 3,4-benzofluorene, phenyl lithium, and 1,5-dibromopentane gave a semisolid hydrocarbon mixture which was purified through its picrate and then oxidized with chromic oxide. Condensation of the crude quinone with *o*-phenylenediamine gave a quinoxaline in 7% over-all yield, which was shown to be identical with the quinoxaline derived from A. This preparation unambiguously establishes the structures of A and B as being II and IV, respectively. Structure V for the quinone is based on the very reasonable assumption that oxidation of IV occurred in the substituted naphthalene ring, as it does in electrophilic substitution reactions of 1,2-dimethylnaphthalene (6, 7, 8). It follows that the quinoxaline has structure VI.

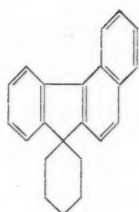
The structures ascribed to B were based on a comparison of its ultraviolet spectrum with those of 3,4-benzofluorene (2) and benzanthrene (3). Although the spectra of the latter two hydrocarbons are quite similar (9, spectra numbers 430 and 436), the difference is sufficient to justify Jones' original assignment (2) of structure IV to B. Before attempting the synthesis of the quinoxaline (VI), 3,4-benzo-9,9-dimethylfluorene (VII) was prepared as a more suitable model. Oxidation gave a quinone which formed a quinoxaline.

<sup>1</sup>Manuscript received March 8, 1960.

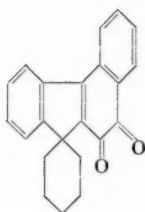
Contribution from the Chemistry Department, the University, Hull, East Yorkshire, England.

<sup>2</sup>I.C.I. Fellow.

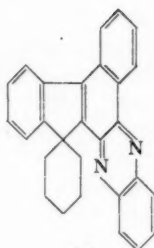
\*The isomeric cyclohexylidene structure has been used (4) but is incorrect since it has been shown (5) that the starting material is 2-cyclohex-1'-enylcyclohexanone.



IV



V

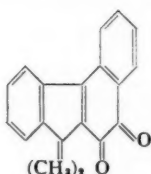


VI

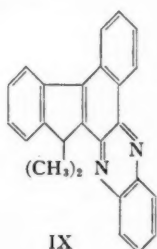
For reasons outlined above, these are given structures VIII and IX, respectively. The ultraviolet spectra of the pairs IV-VII, V-VIII, and IV-IX were almost superposable and the infrared spectra were remarkably similar, even in the fingerprint region.



VII



VIII

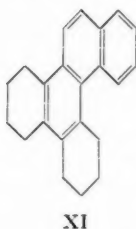
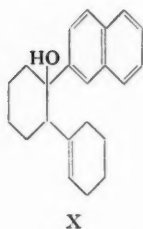


IX

Bergmann and Eschinazi (1) were unable to prepare either A (II) or B (IV) crystalline, and the picrate of A was accompanied by a second, unidentified, picrate. Our original procedure (3) has been repeated but only one picrate (of A) could be isolated. Both A and B are readily obtained crystalline after purification of their picrates. The sample of B examined by Jones (2) was impure since its ultraviolet spectrum showed low intensity bands at wavelengths greater than  $340\text{ m}\mu$  in contradistinction to our crystallized sample. Data presented in the section dealing with spectra (see Experimental) suggests strongly that the impurity was perylene. This could have been formed under the vigorous conditions used for the cyclization by oxidative dimerization (10) of naphthalene present as impurity in the tertiary alcohol (I). It is significant that the sample of B was described (2) as 'yellow'.

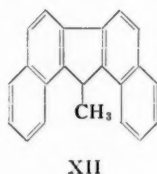
The cyclization described above is of particular interest since a five-membered ring is formed by substitution at a  $\beta$ -naphthyl position although  $\alpha$ -substitution to give a six-membered ring seemed feasible. Similar cyclizations have been reported (11, 12) and it is agreed (4, 11, 12) that they proceed by way of mesomeric carbonium ions, but plausible reasons for the preferred direction of cyclization have not been advanced. The tertiary alcohol (X), isomeric with I, was cyclized to (XI) (3), showing that six-membered rings may be formed by  $\alpha$ -substitution.

Under the influence of stannic chloride, 1,1-diphenylethylene is well known to dimerize, the initial product undergoing further reactions. Wolf (11) has reported that the same reagent cyclizes 1,1-(di- $\alpha,\beta$ -naphthyl)-ethylene to 1,2:5,6-dibenzo-9-methylfluorene, and 1,1-(di- $\alpha,\alpha$ -naphthyl)-ethylene to 1,2:7,8-dibenzo-9-methylfluorene (XII). Under comparable conditions 1,1-(di- $\beta,\beta$ -naphthyl)-ethylene was dimerized. It has now been found



that 1-( $\alpha$ -naphthyl)-1-phenylethylene is recovered unchanged after being heated on the steam bath with stannic chloride, for periods up to 48 hours. A reasonable interpretation of these facts is not available.

The structure of Wolf's hydrocarbon (XII) has been confirmed by synthesis from 1,2:7,8-dibenzofluorenone which, contrary to an earlier report (13), forms an oxime.\*



#### EXPERIMENTAL

##### *3,4-Benzo-5,6,7,8-tetrahydrofluorene-9-spiro-cyclohexane (A, II)*

2-Cyclohex-1'-enyl-1- $\alpha$ -naphthyl-cyclohexanol (I) was prepared as described previously (3). A sample slowly crystallized, recrystallization from hexane giving small prisms, m.p. 102–104° (lit. m.p. 104.0–104.5° (15)). Cyclization with aluminum chloride, using carbon disulphide as solvent, followed by distillation at 1 mm gave a pale yellow gum, which was converted to the dark red picrate, m.p. 163–164° (1, 3). Regeneration of the hydrocarbon by passing a solution of the picrate in benzene through a column of activated alumina gave an easily crystallized product which formed prisms from methanol, m.p. 96–98° (3).

##### *3,4-Benzofluorene-9-spiro-cyclohexane (B, IV)*

Dehydrogenation of a crystallized sample of the preceding hydrocarbon at 300°, using 10% palladium on charcoal as catalyst, gave an oil which was converted to the bright red picrate, m.p. 142–143° (1, 3). Regeneration of the hydrocarbon gave an oil which crystallized after it was cooled with liquid air. Recrystallization from acetone-methanol gave colorless prisms, m.p. 88–90° (3). The yield based on I was 38%.

Oxidation with  $\text{CrO}_3$  in acetic acid gave 3,4-benzofluorene-1,2-quinone-9-spiro-cyclohexane (V), which crystallized as lustrous crimson plates from acetic acid, m.p. 224–225° (1, 3).

##### *14H-Benz[a]indeno[1,2-c]phenazine-14-spiro-cyclohexane (VI)*

The crude quinone (1 g) was boiled for 30 minutes with a solution of *o*-phenylenediamine (3 g) in acetic acid (70 ml). After pouring into dilute hydrochloric acid (500 ml)

\*9-Benzoylanthracene has also been reported not to form an oxime (14) but should do so under the conditions described in the Experimental.



the product was extracted with chloroform. Evaporation left a brown solid which was dissolved in hexane and the solution passed through a column of activated alumina. A bright yellow highly fluorescent band was eluted with benzene-hexane (1:2) and the eluant evaporated. Crystallization from heptane gave bright yellow prisms (0.6 g), m.p. 235–236°. Found: C, 87.15; H, 5.71; N, 7.14. Calc. for  $C_{28}H_{22}N_2$ : C, 87.01; H, 5.74; N, 7.25%.

1,5-Dibromopentane (2 g) was added to a solution of 3,4-benzofluorene (2 g) in ether containing phenyl lithium (from bromobenzene, 10 g). The color of the fluorene anion had disappeared after 8 minutes. Inorganic salts were removed by washing with water and the ether was evaporated to leave an oily hydrocarbon. After purification through the bright red picrate, m.p. 122–136°, the hydrocarbon mixture partly crystallized when seeded with IV. Oxidation with  $CrO_3$  (5 g) in acetic acid followed by condensation with *o*-phenylenediamine gave a quinoxaline, which was purified as described above. Crystallization from heptane gave bright yellow prisms (0.25 g, 7% based on 3,4-benzofluorene), m.p. 232–234°, not depressed by the quinoxaline from B. Found: C, 86.91; H, 5.82. Comparison of infrared spectra confirmed the identity.

#### 3,4-Benzo-9,9-dimethylfluorene (VII)

3,4-Benzofluorene (5 g) was methylated as described for fluorene (16). The oily product was converted to the *picrate*, which crystallized from ethanol as beautiful dark red needles, m.p. 147–149°. Found: C, 63.59; H, 4.14. Calc. for  $C_{26}H_{19}N_3O_7$ : C, 63.42; H, 4.05%.

Decomposition of the picrate on alumina gave an easily crystallized product which formed colorless prisms from acetone-methanol, m.p. 82–83°. Many of the crystals showed extensive twinning. Found: C, 93.65; H, 6.61%. Calc. for  $C_{19}H_{16}$ : C, 93.40; H, 6.60%.

Oxidation with  $CrO_3$  in acetic acid was complete after a few minutes on the steam bath. 3,4-Benzo-9,9-dimethylfluorene-1,2-quinone (VIII) crystallized as lustrous crimson plates from acetic acid, m.p. 216–217.5°. Found: C, 83.03; H, 5.13. Calc. for  $C_{19}H_{14}O_2$ : C, 83.19; H, 5.14%.

#### 1,4,14-Dimethyl-14H-benz[*a*]indeno[1,2-*c*]phenazine (IX)

Prepared and purified as described for VI, the quinoxaline formed bright yellow blades from heptane, m.p. 193–194°. Found: C, 86.70; H, 5.26. Calc. for  $C_{26}H_{18}N_2$ : C, 86.67; H, 5.24%.

#### 1,2:7,8-Dibenzo-9-methylfluorene (XII)

The reaction between ethereal methyl lithium and 1,2:7,8-dibenzofluorenone (17) gave an almost quantitative yield of 1,2:7,8-dibenzo-9-methyl-9-fluorenol, which crystallized from toluene as colorless plates, m.p. 216–218° (not analyzed). The fluorenol (1 g) was reduced by warming with acetic acid (200 ml) and zinc dust (20 g), a few drops of concentrated hydrochloric acid being added every 5 minutes during 30 minutes. The product crystallized from heptane as colorless lustrous plates (0.7 g), m.p. 173–174°, not depressed by an authentic sample of Wolf's hydrocarbon (11). During the preparation of the latter it was noted that stannic chloride from a new bottle did not react with the dinaphthylethylene, but addition of a drop of water initiated the reaction observed by Wolf (11). This experiment was carried out in Ottawa during a prolonged cold spell (–20° F) when the relative humidity was very low.

*1,2:7,8-Dibenzofluorenone Oxime*

The ketone (0.1 g), hydroxylamine hydrochloride (1 g) and dry pyridine (10 ml) were boiled under reflux for 2 hours. The mixture was poured onto ice and hydrochloric acid and the precipitate crystallized from toluene-heptane to give slender orange needles (0.08 g), m.p. 211–212° with decomposition. Found: N, 4.63. Calc. for  $C_{21}H_{13}NO$ : N, 4.74%.

The known oximes of fluorenone and 3,4:5,6-dibenzofluorenone were prepared similarly in excellent yields.

1,1-Diphenylethylene (10 g, f.p. 7–8°) and stannic chloride (25 g) were warmed on the steam bath for 10 minutes. Pouring onto ice and hydrochloric acid precipitated a white solid which crystallized from acetone-methanol as white prisms (5.5 g), m.p. 112–113°, completely identified as 1,1,3,3-tetraphenylbut-1-ene (lit. m.p. 113–114 (18)) by oxidation with  $CrO_3$  to benzophenone (2,4-dinitrophenylhydrazone) and  $\alpha,\alpha$ -diphenylpropionic acid, identical with an authentic sample (19).

1- $\alpha$ -Naphthyl-1-phenylethylene (20) was recovered unchanged in more than 90% yield after it was heated on the steam bath with stannic chloride for periods up to 48 hours.

## SPECTRA

Infrared spectra were obtained using a Unicam SP-100 spectrophotometer with samples prepared as solutions in chloroform and as potassium bromide disks.

Ultraviolet spectra were obtained using a Beckmann DK-2 recording spectrophotometer with ethanol as solvent. The data is collected in Table I, for the hydrocarbons and quinones. The quinoxalines showed peaks at 432, 415, 320, 307, 278, 255, and 229  $m\mu$  (log  $\epsilon$  values not recorded).

TABLE I

Compound					Hydrocarbons						
VII					339	324	314	303	247*	240*	231†
					4.17	4.07	4.13	4.01	4.34	4.5	4.68
IV (3, 21)†					340	325	316	305*	250*		234†
					4.19	4.04	4.05	3.93	4.29		4.61
(2)	436	410.5	384.5		339.5	325	315		Not recorded		
	1.69	1.61	1.38		4.55	4.43	4.45				
Perylene (22)	434†	406†	387†								
	4.6	4.45	4.1								
					Quinones						
VIII	453†	329†	265†			246†					
	3.43	3.89	4.28			4.25					
V (3, 21)†	439	308	264		255*	249					
	3.41	3.80	4.30		4.28	4.26					
(2)	460	333	268			247					
	3.49	3.94	4.32			4.28					

NOTE: The data is presented as  $\lambda(m\mu)/\log \epsilon$ .

\*Shoulder or inflection. †Solvent: cyclohexane. ‡Broad peak.

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# THE REACTION OF 2-CYANO-2-PROPYL FREE RADICALS WITH OXYGEN 2-CYANO-2-PROPYL HYDROPEROXIDE<sup>1</sup>

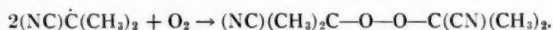
M. TALÂT-ERBEN<sup>2</sup> AND NEVZAT ÖNOL

## ABSTRACT

The reaction with oxygen of cyanisopropyl free radicals generated by the polymerization catalyst 2,2'-azobisisobutyronitrile has been investigated. In xylene, or benzene, as solvent at 55° the products identified are: (1) a new compound, 2-cyano-2-propyl hydroperoxide; (2) acetone cyanohydrin; (3) hydrogen cyanide; (4) cyanogen; (5) acetone; (6) *p*-methyl benzaldehyde (in xylene only); and (7) tetramethylsuccinodinitrile. The hydroperoxide is surprisingly stable; its physical constants are: b.p. 37° C at 1 mm Hg; m.p. -9 to -8°;  $n_D^{20}$  1.4138;  $d_{20}$  1.013 g/ml. In benzene under the same experimental conditions, only a very small amount of the hydroperoxide is obtained, the principal product being acetone cyanohydrin. A free-radical mechanism is proposed. The induced decomposition of the hydroperoxide, which is important in benzene, is almost completely inhibited in the presence of xylene. The new hydroperoxide can be used as a polymerization catalyst at moderately elevated temperatures.

## INTRODUCTION

The thermal decomposition of 2,2'-azobisisobutyronitrile (Porofoor N) has been studied extensively in the absence of oxygen (1, 2). Ziegler *et al.* (3) state that during decomposition in the presence of air, the total pressure of the gas phase does not change, owing to the fact that the increase of pressure due to the nitrogen evolved, is compensated by the equimolecular amount of oxygen taken up simultaneously by the cyanisopropyl radicals produced. These authors postulated the formation of di-(2-cyano-2-propyl) peroxide,



Van Hook and Tobolsky (4), on the other hand, observed that when the azo compound is decomposed in the presence of air, the optical density of the solution becomes higher than in the case in which the decomposition is carried out in an oxygen-free atmosphere, indicating that some peroxides are formed which absorb light in the ultraviolet region. However, neither Ziegler and co-workers nor Van Hook and Tobolsky attempted to isolate these products. Therefore, it would be of interest to investigate this reaction.

## EXPERIMENTAL

The azo compound was recrystallized from benzene, m.p. 101° C with decomposition. The reaction was carried out at 55°, benzene (E. Merck) or xylene (E. Merck) being used as solvent. The solvent was dried with anhydrous sodium sulphate. A continuous stream of tiny bubbles of oxygen was passed at the rate of about 3 liters per hour, through the solution containing 30 g of the azo compound in 300 ml of solvent. The tiny bubbles were produced by forcing the gas to pass through a sintered-glass filter surface, placed at the bottom of the reaction vessel. The oxygen was purified by passage through towers containing soda lime and calcium chloride. The gas leaving the reaction vessel was passed through a reflux condenser to trap the solvent as well as other liquid products that it probably carried with it, then bubbled through a solution of potassium hydroxide to absorb the hydrogen cyanide and cyanogen, which were found to be reaction products (see below). After about 100 hours the reaction was stopped, and the excess of solvent

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was removed by distillation under reduced pressure. The residual solution was extracted 15 to 20 times with 50 ml of distilled water. The combined aqueous solutions were extracted with ether. The ethereal solution was dried with anhydrous sodium sulphate, then evaporated at 60°, until all the ether was removed. The residue from the ether extract, which consisted of a yellowish liquid, was fractionated by vacuum distillation in an all-glass apparatus with a Claisen head, and two fractions were obtained. Fraction A, collected between 60 to 65° at 15 mm Hg, proved to be acetone cyanohydrin, whereas the subsequent fraction B has been identified as 2-cyano-2-propyl hydroperoxide,  $(\text{NC})(\text{CH}_3)_2\text{C}-\text{O}-\text{O}-\text{H}$ .

#### *Identification of Acetone Cyanohydrin*

A sample of fraction A, further purified by fractional distillation, b.p. 62°/15 mm Hg,  $n_D^{20}$  1.3990, boiled at about 110° at atmospheric pressure, and decomposed while boiling. Two products of decomposition were detected: a liquid, trapped by means of a reflux condenser, and a gas absorbed in potassium hydroxide. The liquid, b.p. 51°/76 cm Hg,  $n_D^{20}$  1.3550, formed with 2,4-dinitrophenylhydrazine a crystalline precipitate with a melting point of 126° C. This liquid must, therefore, be acetone. In the potassium hydroxide solution, cyanide was detected (Berlin blue). It follows that fraction A is acetone cyanohydrin. Nitrogen content found (Kjeldahl): 16.07%. Calculated for  $\text{C}_4\text{H}_7\text{ON}$ : 16.46%. Yield: 85 (mole)% in benzene, 20 (mole)% in xylene, based on the azo compound decomposed.

#### *Identification of 2-Cyano-2-propyl Hydroperoxide*

Fraction B is a peroxide. Its high solubility in water suggests that it is a hydroperoxide, rather than a di-(cyano-alkyl) peroxide. This has been confirmed by the following observations. The product from vacuum distillation was further purified by fractional crystallization. On cooling to -10°, colorless crystals were obtained. By use of the analytical procedure of Vaughan and co-workers (5) a molecular weight of 105 was found, assuming that only one  $-\text{O}-\text{O}-$  group is contained in the molecule. A cryoscopic molecular weight determination in benzene gave a value of 95. The two results compare well with the theoretical molecular weight of 101, corresponding to the structure  $(\text{NC})(\text{CH}_3)_2\text{C}-\text{O}-\text{O}-\text{H}$ , and they are incompatible with the structure  $(\text{NC})(\text{CH}_3)_2\text{C}-\text{O}-\text{O}-\text{C}(\text{CH}_3)_2(\text{CN})$ . Nitrogen content found (Kjeldahl): 13.52%. Calculated for  $\text{C}_4\text{H}_7\text{O}_2\text{N}$ : 13.86%. This product must, therefore, be isobutyronitrile hydroperoxide of at least 96% purity. Its physical constants are: b.p. 37°/1 mm Hg, m.p. -9 to -8°,  $n_D^{20}$  1.4138,  $d_{20}$  1.013 g/ml.

This hydroperoxide is surprisingly stable. The pure material decomposes only above 120°. Yield in xylene: 46 (mole)% with respect to the azo compound; in benzene the yield is negligible (2 (mole)%).

#### *Polymerization Experiment*

About 0.3 gram of hydroperoxide was added to 15 ml of methacrylonitrile in a test tube, and heated at 80°. Approximately 20% of the monomer polymerized in 3 hours. This indicates that the hydroperoxide can be used as a polymerization catalyst.

#### *Detection of Hydrogen Cyanide, Cyanogen, and Acetone*

The alkaline solution, through which the oxygen was bubbled after it had left the reaction vessel, was analyzed, and both cyanide and cyanate were found. The former was characterized by the formation of Berlin blue, and the latter by the pyridine test (6). The amount (in moles) of cyanide formed is higher than that of cyanate, indicating

that not only  $(\text{CN})_2$  but  $\text{HCN}$  also is a reaction product. The excess of solvent, which was removed immediately before extraction with ether, was found to contain an appreciable amount of acetone (color test with salicylaldehyde).

#### *Tetramethylsuccinodinitrile*

The residue from water extraction was left standing overnight at  $-20^\circ$ . A large amount of tetramethylsuccinodinitrile crystals were obtained, m.p.  $168^\circ \text{C}$ .

#### *Isolation of p-Methylbenzaldehyde*

After tetramethylsuccinodinitrile (TMSDN) crystals were separated, the residual solution was vacuum-distilled to remove the solvent; the brown, viscous residue was left standing at  $-20^\circ$  overnight, and more TMSDN crystals precipitated. The viscous phase was subjected to a vacuum distillation at  $40^\circ$  (bath temperature), the products being collected in a flask immersed in a dry ice and acetone mixture. At first, more solvent (xylene) and water were collected. The next fraction was refluxed with 30% sulphuric acid in order to hydrolize and dissolve the nitriles (if any). Then, the dark oily residue was purified by steam distillation, and a light yellowish liquid was obtained. This had a strong odor of bitter almond, and a refractive index of 1.548. It proved to be an aldehyde (mirror test). The refractive index is very close to that of *p*-methylbenzaldehyde. Therefore, it is reasonable to assume that this is an oxidation product of the solvent (xylene) sensitized by the free radicals. In fact, it is known that if, under ultraviolet illumination, oxygen is bubbled through toluene for a long time some benzaldehyde is obtained (8). This identification is further supported by the fact that this product was not found in the residues from the runs in which benzene was used as solvent.

### DISCUSSION

The nature and diversity of the reaction products which have been identified in this work show that the reaction of cyanisopropyl radicals with oxygen is a very complicated one. Di-(2-cyano-2-propyl) peroxide, the formation of which was postulated by Ziegler *et al.* (3), has not been found in the present work. This could mean that this peroxide is thermally unstable at the operating temperature, or it is very sensitive to the radical-induced decomposition caused by the free radicals which are present at relatively high concentrations during the entire course of the reaction. Undoubtedly, this peroxide must be much more unstable than its unsubstituted analogue, di-tertiary butyl peroxide, owing to the electron-attracting character of the two nitrile groups in the molecule. Its main decomposition products would be acetone and  $\cdot\text{CN}$  free radicals. The former has actually been detected as shown in the experimental part; the recombination product of the latter, cyanogen, has also been identified. The fact that the hydroperoxide is not obtained when benzene is used as solvent could be explained by the greater stability of the benzene molecule with respect to hydrogen abstraction by the  $(\text{NC})(\text{CH}_3)_2\text{C}-\text{O}-\text{O}\cdot$  radicals. Consequently, these radicals would have a longer mean life in benzene; this would favor their combination with other radicals. Therefore, a transient formation of di-cyanisopropylperoxide is more probable in benzene than in xylene. This conclusion could be correlated with the observation that in some runs with benzene, in which the reaction was stopped at an early stage owing to an experimental difficulty of some kind, an explosive reaction took place during the vacuum distillation of the reaction mixture. Another possible explanation is that the hydroperoxide does actually form in benzene by hydrogen abstraction from other sources (molecules or free radicals available), but in the reaction medium which contains a high concentration of free radicals, it undergoes



a fast-induced decomposition in this particular solvent. In fact, we found that the hydroperoxide which, when pure is very stable up to 120° C, decomposes with a measurable rate in benzene at temperatures as low as 75° C, in the presence of the azo compound. On the other hand, we found that the decomposition of the hydroperoxide in the presence of the azo compound is negligible at the same temperature when xylene is used instead of benzene.

The experimental evidence available does not seem to permit a final conclusion concerning the two alternatives. However, it can be concluded that the nature of the reaction products identified in this work indicates that there must be a complete analogy between the mechanisms of the thermal decomposition of the cyano-alkyl peroxides and that of the corresponding alkyl peroxides. In other words, a reaction scheme similar to that proposed by Vaughan *et al.* (7), for the liquid phase decomposition of *t*-butylhydroperoxide, can be used to account for the decomposition of cyanisopropyl hydroperoxide, if it is assumed that dismutation of cyanisopropoxy radicals,  $(\text{NC})(\text{CH}_3)_2\text{C}-\text{O}\cdot$ , produced by cleavage of the O—O bond, gives  $\cdot\text{CN}$  free radicals. A similar mechanism would be applicable to the more unstable di-(cyanisopropyl) peroxide.

An experimental investigation of the kinetics of the thermal decomposition of cyanisopropylhydroperoxide, and its properties as a polymerization catalyst, is under way in these laboratories, and will be the subject of a subsequent publication.

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# THE ELECTRON SPIN RESONANCE ABSORPTION SPECTRA OF SEMIQUINONE IONS

## PART I. THE HYPERFINE SPLITTING DUE TO ALKOXY GROUPS<sup>1</sup>

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### ABSTRACT

The electron spin resonance absorption spectra of semiquinone ions with alkoxy groups have been examined and compared with those with substituted alkyl groups. The splitting constant for the alkoxy protons has been found to be about one-half that of alkyl protons in the corresponding free radical. Hyperfine splittings due to methoxy, ethoxy, and isopropoxy protons have been demonstrated using the semiquinone ions formed by oxidation of alkyl gallates. The available evidence suggests that, in accounting for the hyperfine splitting due to alkyl protons, spin polarization is as important as electron delocalization.

### INTRODUCTION

The electron spin resonance (e.s.r.) absorption spectra of semiquinone ions have been examined extensively by many workers. The rather simple structure of the free radicals of this kind makes possible the analysis of the hyperfine structure of the observed resonance absorption spectra. It has been shown by the studies of the methyl-substituted benzo- and naphtho-semiquinone ions (1, 2) that both the ring and the methyl protons contribute to the hyperfine splitting in comparable magnitude. The cause of the methyl proton splitting has been ascribed to hyperconjugation, and the details have been accounted by the molecular orbital and the valence bond theories of hyperconjugation (3, 4). Proton hyperfine splitting for more complicated substituents has been described in some cases. Hyperfine splitting due to *tert.*-butyl protons in benzosemiquinone ions has been observed by Hoskins (5) and by Fraenkel (6). The three triplets found in the spectrum of the semiquinone ion formed by the oxidation of *n*-propyl gallate may be assigned (7) to two ring protons and two *n*-propyl protons.

Here we wish to present the results of a study of the contribution of alkoxy protons to the hyperfine structure of the e.s.r. absorption spectra of some semiquinone ions. With the view to ascertaining the effect of the oxygen atoms we examined the spectra of the 2,5-dimethoxy- and 2,5-diethoxy-*p*-benzosemiquinone ions, and also the 3,3',5,5'-tetramethyl-*p*-biphenosemiquinone ion, and compared these with those of the 2,5-dimethylbenzo- and 3,3',5,5'-tetramethyl-*p*-biphenosemiquinone ions. Secondly, to demonstrate the contribution of methoxy, ethoxy, and isopropoxy protons, we examined the semiquinone ions formed by the oxidation of various alkyl gallates.

The hyperfine splitting observed in the e.s.r. spectra of free radicals is caused by the interaction between nuclei with a magnetic moment, and an unpaired electron, through direct dipole-dipole forces, and also through the isotopic Fermi interaction between the nuclear magnetic moment and the electron-spin magnetic moment. Free radicals in solution can show only hyperfine splitting due to the latter interaction, because the rapid tumbling of the molecule averages out the anisotropic dipolar interaction (8). The magnitude of the splitting due to the Fermi interaction is proportional to the spin density at the nucleus. If we adopt a single configurational molecular orbital description, the spin density will be replaced by the unpaired electron density. It has been shown that

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the magnitude of ring proton splitting is approximately proportional to the density of the unpaired  $\pi$ -electron in the aromatic carbon atom (9), and a similar relation holds for the methyl protons (4).

The spin Hamiltonian for an organic free radical of the semiquinone type may be written as

$$[1] \quad H = g\beta \mathbf{H} \cdot \mathbf{S} + \sum_i A_i (\mathbf{S} \cdot \mathbf{I}_i)$$

which has eigen values

$$[2] \quad E = g\beta H M_S + \sum_i A_i M_S M_{I_i}.$$

For the transitions  $(M_S \rightarrow M_S' \pm 1)(M_I \rightarrow M_I)$  this yields, for the strong field case, the frequencies

$$[3] \quad \nu = \frac{1}{h} \left\{ g\beta M + \sum_i A_i M_{I_i} \right\}.$$

The subscript  $i$  refers to the nucleus which is coupled to the electron spin. The summation is taken over all such nuclei in the radical. The nuclear magnetic quantum number  $M_{I_i}$  takes on the values,  $I_i, I_i+1, \dots, -I_i$ . There are  $2I_i+1$  such values. If the coupling constants for all the nuclei are equal (i.e.  $A_1 = A_2 \dots = A_i$ ) the hyperfine splitting constant for each line will be  $AM/g\beta$  where  $M$  is the total magnetic quantum number. In the case of protons, the spin is  $\frac{1}{2}(\hbar/2\pi)$ ; therefore the absorption spectrum for a free radical with  $N$  equivalent proton consists of  $N+1$  hyperfine components with the relative intensities given by the binomial distribution  $1:N:N(N-1)/2: \dots N!/k!(N-k)!: \dots :N:1$ .

#### EXPERIMENTAL

2,5-Dimethoxy- and 2,5-diethoxy-*p*-benzoquinones were prepared by the reaction of the corresponding alcohols with benzoquinone, using anhydrous zinc chloride as a catalyst (10). The compounds were purified by vacuum sublimation. By reduction with sodium dithionite, these two quinones, on dissolving in a mixture of pyridine and 2 *M* KOH (1:1 by volume), give fairly stable free radicals. It was hoped to stabilize the monomeric form of the semiquinone ions by the use of pyridine (11). 3,3',5,5'-Tetramethyl- and 3,3',5,5'-tetramethoxy-*p*-biphenols were prepared from the quinones starting from 2,6-dimethylphenol and 2,6-dimethoxyphenol, respectively (12, 13). These biphenols were purified by recrystallization from ethanol and finally by sublimation in vacuum. The semiquinone ions were obtained by air oxidation of the biphenols dissolved in the above-mentioned mixed solvent. The esters of gallic acid were prepared by the standard methods of esterification using sulphuric acid or hydrogen chloride gas as a catalyst (14, 15). The compounds were finally sublimed in a vacuum. The semiquinone ions were obtained by air oxidation of the esters dissolved in a mixture of ethanol and 2 *M* KOH (1:1 by volume). These free radicals could not be found when the parent compound was dissolved in a mixture of pyridine and 2 *M* KOH. The choice of ester is of great advantage in the preparation of the samples with the desired alkoxy groups. However, the hydrolysis during the course of the measurements could not be prevented (see the following section).

An e.s.r. spectrometer with a transmission cavity was used at room temperature, as described previously (16). The spectra shown in this paper are the first derivative of the

actual absorption lines. The estimated error for the splitting constants is about 0.02 gauss provided the lines are sharp enough. The intensity of the magnetic field increases from left to right in all the figures.

## RESULTS AND DISCUSSION

### *2,5-Dimethoxy- and 2,5-Diethoxy-*p*-benzosemiquinone Ions*

2,5-Dimethoxy-*p*-benzosemiquinone ion (Ia) shows seven main lines with a hyperfine splitting of 1.05 oersteds (Fig. 1). Although the asymmetric pattern suggests the overlap of the spectra due to other free radicals from impurities or reaction products, further splitting of each line into a triplet could be observed except for the outermost lines (Fig. 2). The 2,5-diethoxy-*p*-benzosemiquinone ion (Ib) gives a five-line spectrum with a spacing of 1.17 oersteds (Fig. 3). Apparently the major splitting can be attributed to

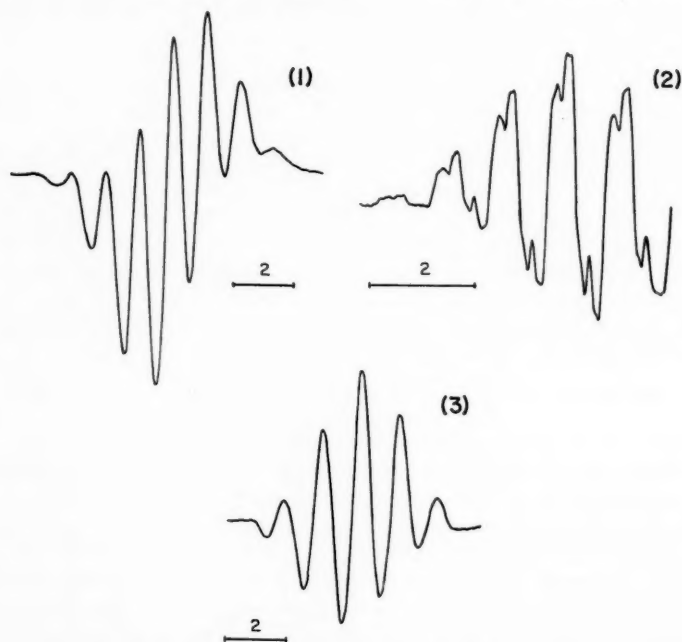
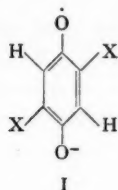


FIG. 1. First derivative of e.s.r. absorption spectrum of the 2,5-dimethoxy-*p*-benzosemiquinone ion (Ia).

FIG. 2. First derivative of a part of e.s.r. absorption spectrum of semiquinone ion (Ia) under higher resolution.

FIG. 3. First derivative of e.s.r. absorption spectrum of the 2,5-diethoxy-*p*-benzosemiquinone ion (Ib).

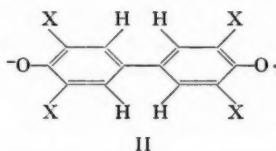
hyperfine coupling with the alkoxy protons and the minor one of 0.30 oersted found in the methoxy derivative can be ascribed to coupling with the ring protons. In the case of the 2,5-dimethyl-*p*-benzosemiquinone ion examined by Venkataraman and Fraenkel (1), the splitting constant for the ring protons was reported to be 1.83 oersteds and that for the methyl protons 2.26 oersteds. The considerable decrease of the splitting constant of the ring protons resulting from the change of the substituent from alkyl to alkoxy suggests the possible preferential localization of the unpaired electron on the oxygen atoms in the alkoxy groups. Nevertheless, the splitting constant of the alkoxy protons is also less than that of the alkyl protons.

(a)  $X = \text{CH}_3\text{O}$ (b)  $X = \text{CH}_2\text{CH}_2\text{O}$ 

I

*3,3',5,5'-Tetramethyl- and 3,3',5,5'-Tetramethoxy-*p*-biphenosemiquinone Ions*

The 3,3',5,5'-tetramethyl-*p*-biphenosemiquinone ion (IIa) has four ring protons and 12 methyl protons; therefore, if the two benzene nuclei are equivalent five sets of 13 lines are to be expected. Only 21 lines with equidistant spacings were detected because of overlap and small intensity of some of the lines (Fig. 4). The values of the splitting constants, 2.34 oersteds for the ring protons, and 0.78 oersted for the methyl protons, seem to give the pattern which is most consistent with the experimental one. The following intensity ratio is predicted: 1:12:66:224:543:1056:1810:2844:4059:5240:6252:7008:7306:7008:6252:5240:4059:2844:1810:1056:543:224:66:12:1. Among these 25 lines the two at each end of the spectrum are too weak to be detected.

(a)  $X = \text{CH}_3$ (b)  $X = \text{CH}_2\text{O}$ 

II

The 3,3',5,5'-tetramethoxy-*p*-biphenosemiquinone ion (IIb) has the same number of ring and methyl protons as the tetramethyl derivative. However, the total spread of the spectrum was found to be less than one third of that of the tetramethyl derivative. The observed 13-line spectrum (Fig. 5) can be explained with a splitting constant of 0.49

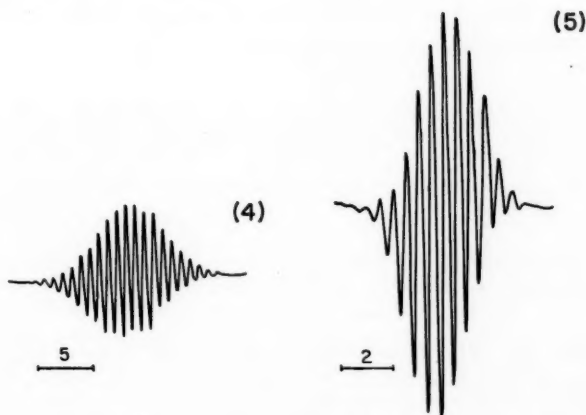


FIG. 4. First derivative of e.s.r. absorption spectrum of the 3,3',5,5'-tetramethyl-*p*-biphenosemiquinone ion (IIa).

FIG. 5. First derivative of e.s.r. absorption spectrum of the 3,3',5,5'-tetramethoxy-*p*-biphenosemiquinone ion (IIb).

oersted for both the ring and the methoxy protons. The predicted intensity ratio is 1:16:120:560:1820:4368:8008:11440:12870:11440:8008:4368:1820:560:120:16:1. Again the two lines at each end are expected to be too low in intensity to be detectable. The decrease of the splitting constant of the ring protons is again observed on changing the substituent from methyl to methoxy.

TABLE I  
Proton splitting constants in alkyl and alkoxy derivatives  
of *p*-benzo- and *p*-biphenosemiquinone ions

Semiquinone ion	Proton splitting constant in oersteds	
	<i>a</i> (ring)	<i>a</i> (alkyl or alkoxy)
I with X = H	2.37*	—
I with X = CH <sub>3</sub>	1.83†	2.26†
Ia	0.30	1.05
Ib	?	1.17
IIa	2.34	0.78
IIb	0.49	0.49

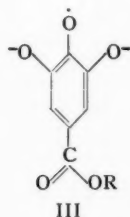
\*See references 1 and 7.

†See references 1 and 3.

Later work (see Part III of this series) has, however, indicated that in *p*-biphenosemiquinone salts the unpaired electron density given by the simple LCAO-MO method for carbon atom *a* (adjacent to the C—O bond) is 1.5, or more, times larger than that on carbon atom *b*, regardless of the magnitude of the coulomb integral for the oxygen atoms in the range of  $\alpha_o = \alpha_c$  to  $\alpha_c + \beta_{cc}$ . This permits an alternative assignment of 0.78 oersted for the ring protons and 1.56 oersteds for the methyl protons. The following intensity ratios result and the 21 lines could be those which are not enclosed in parentheses: (1, 4, 18, 52) 139, 312, 628, 1144, 1881, 2860, 3982, 5148, 6171, 6864, 7128, 6864, 6171, 5148, 3982, 2860, 1881, 1144, 628, 312, 139 (52, 18, 4, 1).

#### Semiquinone Ions from Gallic Acid and Alkyl Gallates

The spectrum of the semiquinone ion (IIIa) formed by oxidation of gallic acid has been reported by Adams, Blois, and Sands (7). The two ring protons give a triplet with a splitting of 1.07 oersteds and a *g*-value of 2.00489.



(a) R = e<sup>-</sup>

(b) R = CH<sub>3</sub>

(c) R = CH<sub>3</sub>CH<sub>2</sub>

(d) R = (CH<sub>3</sub>)<sub>2</sub>CH

The semiquinone ion (IIIb) from methyl gallate gives 10 lines (Fig. 6). The center lines of the expected 12-line spectrum overlap to give a theoretical pattern with an intensity ratio 1:3:3:4:9:9:4:3:3:1. In Fig. 6, the third, the sixth, and the ninth lines from left to right do not follow the above-mentioned ratio. The intensity of these three



lines, compared with the others, increases on standing and this anomaly can be attributed to the presence of a triplet of slightly lower  $g$ -value from gallic acid formed by hydrolysis. The splitting constants for the ring and the methyl protons are estimated as 1.14 and 0.38 oersteds, respectively.

The semiquinone ion (IIIc) from ethyl gallate shows three triplets as expected (Fig. 7). The predicted intensity ratio is 1:2:1:2:4:2:1:2:1. The deviation from the theoretical pattern again suggests the presence of the semiquinone ion from the free acid. Although the third line of the triplet due to gallic acid overlaps nearly perfectly with the eighth line due to the ethyl ester, the resolution of the other two lines becomes better on standing for  $\frac{1}{2}$  hour. As we can see in Fig. 8, the ester has a slightly higher  $g$ -value than the acid.

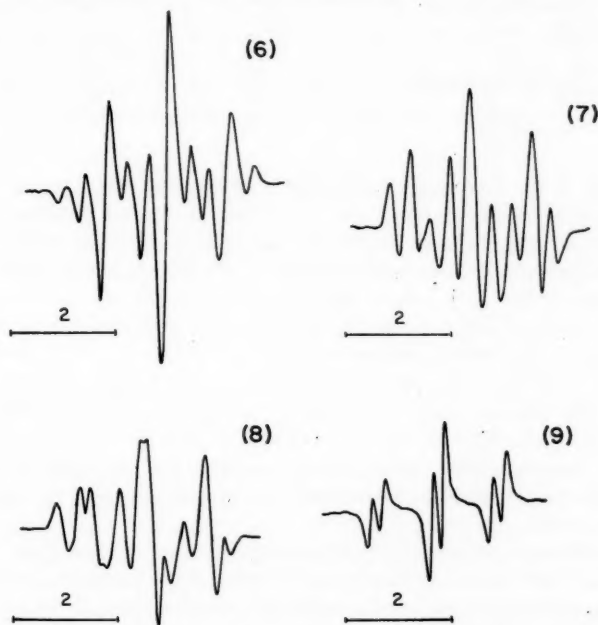


FIG. 6. First derivative of e.s.r. absorption spectrum of the semiquinone ion (IIIb) from methyl gallate.

FIG. 7. First derivative of e.s.r. absorption spectrum of the semiquinone ion (IIIc) from ethyl gallate.

FIG. 8. First derivative of e.s.r. absorption spectrum of the semiquinone ions from hydrolyzed ethyl gallate.

FIG. 9. First derivative of e.s.r. absorption spectrum of the semiquinone ion (IIId) from isopropyl gallate.

The splitting constants are 1.12 oersteds for the ring protons and 0.36 oersted for two of the ethyl protons. The hyperfine splitting due to the other three protons in the ethyl group is too small to be resolved. *n*-Propyl gallate on oxidation gives essentially the same pattern as the ethyl ester. Adams, Blois, and Sands (7) reported two splitting constants, 1.13 and 0.38 oersteds, and a  $g$ -value of 2.00490. Our values for the ethyl ester are in good agreement with those for the *n*-propyl ester within the limit of the experimental errors.

The semiquinone ion (IIId) from isopropyl gallate shows three doublets (Fig. 9). This

ester is fairly stable in an alkaline medium and the sample, from which unreacted acid was carefully removed by sublimation in vacuum, does not show the signals due to gallic acid. The splitting constants are estimated as 1.13 oersteds for the ring protons and 0.24 oersted for one proton in the isopropyl group.

TABLE II  
Proton splitting constants in semiquinone ions from gallic acid and alkyl gallate

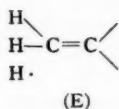
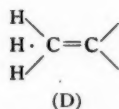
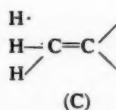
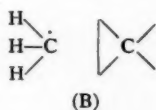
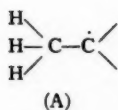
Semiquinone ion	Proton splitting constant in oersteds	
	<i>a</i> (ring)	<i>a</i> (alkyl)
IIIa	1.07*	—
IIIb	1.14	0.38
IIIc	1.12	0.36
III with R = <i>n</i> -propyl	1.13*	0.38*
IIId	1.13	0.24

\*See reference 7.

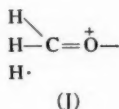
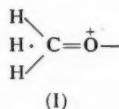
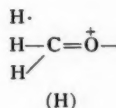
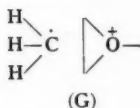
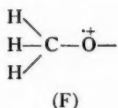
The magnitude of the ring proton splitting in these four esters seems to be constant regardless of the kind of alkyl group; however, it must be noted that the splitting due to the isopropyl proton is found to be about two thirds of those of the methyl and the ethyl protons. The semiquinone ion can be considered as the gallate ion with one positive hole. The small increase of the ring proton splitting by esterification shows that the ability of the negatively charged carbonyl group to attract the positive hole is higher, but only slightly, than that of the neutral carboalkoxy group.

Recently Müller and his collaborators (17) have compared the hyperfine splitting due to the methoxy, the ethoxy, and the isopropoxy protons observed for the alkoxy-2,6-di-*tert*.-butyl-phenoxy radicals. The splitting constants have been found to be 1.6 oersteds for the methoxy and the ethoxy protons and 1 oersted for the isopropoxy proton. The relative magnitude of the splitting constants of these protons is in very good agreement with the present results.

Based on the above experimental results, we can conclude that there is no essential difference between alkyl and alkoxy protons as to their contribution to hyperfine splitting and the effect of alkoxy protons can be ascribed to hyperconjugation. In the molecular orbital theory of hyperconjugation, the  $\pi$ -character of the orbitals in methyl and methylene groups can be found by the use of hydrogen group orbitals (18, 19). The spin densities on the methyl protons have been calculated by Bersohn (3) by taking into account the delocalization of the unpaired electron onto the methyl group. He found general agreement between the calculated and the observed splitting constants in a number of methyl-substituted benzosemiquinone ions; however, the orbital of isopropyl hydrogen has no  $\pi$ -character in this sense. This delocalization of unpaired electron means there is a charge transfer to methyl group, as the unpaired electron in the semiquinone ions is accompanied by a positive hole. In the valence bond theory, hyperconjugation can be understood to mean the introduction of unconventional pairing schemes or spin polarization of the bonds in a methyl group without any accompanying transfer of charge. McLachlan (4) has explained the hyperfine splitting due to methyl protons by considering the following resonance structures and concluded that spin polarization mechanism may be at least as important as electron delocalization in accounting for the hyperfine splitting due to methyl protons.



The application of the valence bond theory can be extended to methoxy group by considering analogous resonance structures. In the methoxy group the oxygen atom with a positive hole takes the place of a trigonal carbon atom in a methyl group. Therefore, the resonance structures H, I, J are probably less important than the structures C, D, E. We may expect that the electronic interaction between the alkyl protons and the oxygen



atom in the alkoxy group is less than that between the alkyl protons and the carbon atom to which the alkyl group is attached. The behavior of two ethyl protons and one isopropyl proton can be explained similarly. We may attribute the difference between the proton splitting constants for methyl and isopropyl groups to the presence of electron delocalization in the former group. In the case of the isopropyl derivative there is the additional possibility that steric hindrance may cause part of the change observed.

#### ACKNOWLEDGMENT

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# THE ELECTRON SPIN RESONANCE ABSORPTION SPECTRA OF SEMIQUINONE IONS

## PART II. THE HYPERFINE SPLITTING DUE TO AMINO GROUPS<sup>1</sup>

Y. MATSUNAGA<sup>2</sup> AND C. A. McDOWELL

### ABSTRACT

The electron spin resonance absorption spectra of amino-substituted *p*-benzosemiquinone ions have been examined. The hyperfine splittings due to the amino protons and the amino nitrogen atom have been demonstrated. It has been found that the magnitude of the hyperfine splitting constants due to these two kinds of nuclei depends very much on the nature of the free radical.

### INTRODUCTION

Though the hyperfine splitting due to a nitrogen atom has been reported in the electron spin resonance (e.s.r.) of a number of organic-free radicals, the hyperfine splitting of the amino nitrogen atom and protons is not yet clear. The nuclear moment of  $N^{14}$  is one, so we can expect one  $N^{14}$  nucleus to cause a splitting of the resonance absorption into a triplet. 1,1-Diphenyl-2-picrylhydrazyl and its analogues (1), di-*p*-anisyl-nitrogen oxide (2), and cyano-di-*tert*-butyl-phenoxyl (3) are the examples of the neutral free radicals which show the  $N^{14}$  splitting. Hyperfine splittings for both the  $N^{14}$  in, and out of, the aromatic ring in positively charged free radicals have been demonstrated in the cases of the phenazine semiquinone ion (4), and triarylaminium ions (5). Nitrobenzene anion (6), and the semiquinone ion from 3-nitrophthalic anhydride (7), show the hyperfine splitting due to  $N^{14}$  in the nitro group. Wurster's blue ions are the only kinds of free radicals with amino groups already studied (8, 9). Unlike those in the above-mentioned free radicals (10) the nitrogen atoms in these positively charged free radicals do not contribute to the hyperfine structure. Therefore, it seemed of interest to examine the hyperfine splitting due to the amino group in the other kind of free radicals. For this purpose, the negatively charged semiquinone ions formed by reduction of 2-amino-5-hydroxy-3,6-dichloro-*p*-benzoquinone; 2,5-diamino-3,6-dichloro-*p*-benzoquinone; 2,5-dianilino-3,6-dichloro-*p*-benzoquinone; and 2,5-di(*N*-piperidyl)-3,6-dichloro-*p*-benzoquinone have been chosen because of the lack of other substituents, which can contribute to hyperfine splitting. Although chlorine has a nuclear moment of spin, this splitting is known too small to be resolved (11).

### EXPERIMENTAL

The parent quinones were prepared starting from chloranil by the methods described in the references. 2-Amino-5-hydroxy-3,6-dichloro-*p*-benzoquinone was prepared by reaction with ammonia in water (12). 2,5-Diamino-3,6-dichloro-*p*-benzoquinone was prepared by the reaction with ammonia in absolute ethanol (13). 2,5-Dianilino-3,6-dichloro-*p*-benzoquinone and 2,5-di(*N*-piperidyl)-3,6-dichloro-*p*-benzoquinone were obtained by the reaction with aniline and piperidine in ethanol, respectively (13, 14). By reduction with sodium dithionite, these quinones on dissolving in a mixture of pyridine, ethylene glycol, and 2 *M* KOH (1:2:1 by volume) give fairly stable free radicals. Pyridine was used with the hope of improving the solvating power and of stabilizing the mono-

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meric form of semiquinone ion (15). The use of ethylene glycol or glycerol has been recommended by Hausser (16). The high viscosity of these compounds contributes to the resolution of the spectra. The solubility of 2,5-di(N-piperidyl)-3,6-dichloro-*p*-benzoquinone in the above-mentioned mixed solvent was found too small; therefore, the concentrated pyridine solution of the quinone was diluted with the mixed solvent containing the reducing reagent.

The e.s.r. absorption of these semiquinone ions was examined at room temperature at a frequency of 9 kMc/s as described previously (17).

### RESULTS AND DISCUSSION

The semiquinone ion (I) from 2-amino-5-hydroxy-3,6-dichloro-*p*-benzoquinone gives three triplets as expected from the presence of one amino nitrogen and two protons (Fig. 1). The intensity ratios are 1:2:1:1:2:1:1:2:1; therefore, we can confidently assign the major splitting to the amino nitrogen and the minor one to the amino protons. The former splitting constant is estimated as 2.5 oersteds and the latter as 0.6 oersted. It must be noted that the magnitude of the amino proton splitting is only about one fourth of that of the amino nitrogen splitting.

The semiquinone ion (II) from 2,5-diamino-3,6-dichloro-*p*-benzoquinone shows a 13-line spectrum (Fig. 2). If the splitting constant of the amino nitrogen is nearly twice,

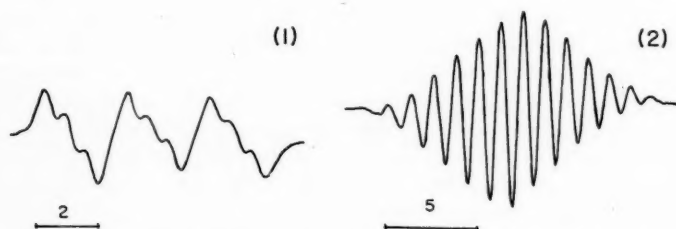
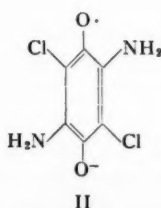
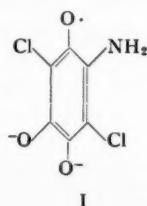


FIG. 1. First derivative of e.s.r. absorption spectrum of the semiquinone ion (I) from 2-amino-5-hydroxy-3,6-dichloro-*p*-benzoquinone.

FIG. 2. First derivative of e.s.r. absorption spectrum of the semiquinone ion (II) from 2,5-diamino-3,6-*p*-benzoquinone.

or one half of that of the amino protons, we can expect 13 lines with the relative intensities 1:4:8:12:16:20:22:20:16:12:8:4:1 or 1:2:7:10:19:20:26:20:19:10:7:2:1. The observed pattern seems to be in agreement with the former. The splitting constants of the nitrogen and the protons are 2.3 oersteds and 1.15 oersteds, respectively. In this case, the nitrogen splitting is a little smaller than that of the semiquinone ion (I) and the proton splitting is increased by a factor of two.





The semiquinone ion (III) from 2,5-dianilino-3,6-dichloro-*p*-benzoquinone has two amino nitrogen atoms and two amino protons. The contribution from two phenyl groups is not expected to be resolvable. As shown in Fig. 3, seven lines with a spacing of 1.1 oersteds are detected. If these seven lines are the whole of the spectrum, the splitting constants of the amino nitrogens and the amino protons must be of the same magnitude (1.1 oersteds) and the intensity ratio must be 1:4:8:10:8:4:1. The resolution of this spectrum is not good, because of the weak concentration of the free radical, and the use of high modulation of the magnetic field. Therefore, we may have missed the outermost weak line at each side. In such a case, the predicted intensity ratio is 1:2:5:6:8:6:5:2:1. The magnitude of the amino proton splitting becomes 2.2 oersteds, namely twice that of the amino nitrogen splitting. The latter values are probably more reasonable.

The semiquinone ion (IV) from 2,5-di(*N*-piperidyl)-3,6-dichloro-*p*-benzoquinone gives nine lines with an equidistant spacing of 1.2 oersteds (Fig. 4). The eight protons attached

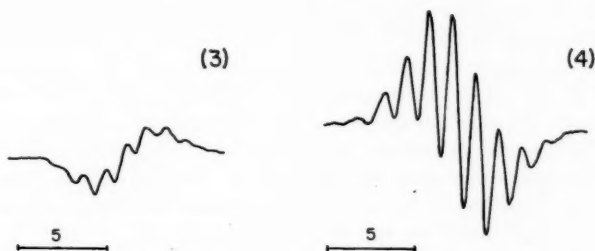


FIG. 3. First derivative of e.s.r. absorption spectrum of the semiquinone ion (III) from 2,5-dianilino-3,6-dichloro-*p*-benzoquinone.

FIG. 4. First derivative of e.s.r. absorption spectrum of the semiquinone ion (IV) from 2,5-di(*N*-piperidyl)-3,6-dichloro-*p*-benzoquinone.

to the carbon atoms adjacent to the nitrogen atoms in two piperidyl rings can be expected to contribute by hyperconjugation to hyperfine splitting with the intensity ratio 1:8:28:56:70:56:28:8:1. Therefore, the observed nine lines can be assigned to these eight protons and the contribution from two piperidyl nitrogen atoms must be too small to be resolved. The magnitude of the proton splitting in the present semiquinone ion must be, at least, several times larger than that of the nitrogen splitting.

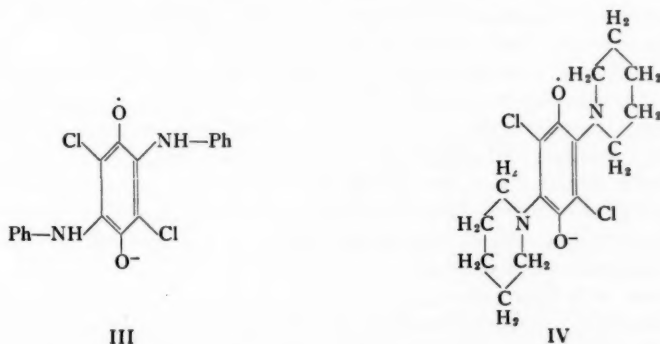


TABLE I  
Splitting constants of nitrogen and proton in amino derivatives  
of 3,6-dichloro-*p*-benzosemiquinone ion

Semiquinone ion	Splitting constants in oersts		
	$a_N$	$a_H$	$a_N/a_H$
I	2.5	0.6	4
II	2.3	1.15	2
III	1.1	2.2 (or 1.1)	1/2 (or 1)
IV	?	1/2	?

The present results show clearly that the amino nitrogen can contribute to hyperfine splitting. The assumption made by McLachlan (10) that the nitrogen atoms contribute no structure as  $N^{14}$  has a quadrupole moment which links its spin orientation to the molecular rotation cannot be considered as general for amino group in organic-free radicals. However, as summarized in Table I, the ratios of the splitting constants of the amino (probably and the alkylamino) protons to those of the amino nitrogen depend considerably on the nature of the molecule. Although the number of the radicals examined is quite small, the increase of the amino proton splitting constant seems to be accompanied by a decrease in the amino nitrogen splitting. This suggestion is consistent with the observation on Wurster's blue ions. For example, in the free radical from tetramethyl-*p*-phenylenediamine, the dimethylamino proton splitting has been reported as large as 7.4 oersts and no nitrogen splitting has been detected (9).

According to theory, the hyperfine splitting is proportional to the Fermi contact term and the magnitude of this Fermi interaction is proportional to the spin density at the nucleus. The unpaired electron in our semiquinone ions is supposed to be in a  $\pi$ -orbital which has a node in the plane of the molecule. The unpaired electron must have some probability of interacting with the *s*-orbitals of hydrogen and nitrogen. It has been shown that  $\sigma$ - $\pi$  interaction is responsible for the hyperfine splitting due to ring protons. The magnitude of the hyperfine splitting is approximately proportional to the spin density in the  $\pi$ -orbital of the neighboring aromatic carbon atom (18). This relation has been supported by a number of experiments (19). The geometrical configuration of the CH group can be considered to be nearly same in every hydrocarbon. Nevertheless, this proportionality constant has been found to depend on the size of aromatic molecule and also on the sign of the charge by the experiments on hydrocarbon negative and positive ions. Therefore, we may expect that the magnitude of hyperfine splitting depends strongly on the nature of the electronic configuration of the group concerned.

The complete planarity of the amino group with the aromatic nucleus favors resonance stabilization. On the other hand, some energy will be required to change the hybridization at the nitrogen atom from the tetrahedral character in aliphatic amines to the trigonal type. We must consider also steric effects in some cases. By compromise between these factors, it seems probable that the geometrical and the electronic configurations of the amino group can be modified by a small change in the nature of the molecule. Consequently, a considerable change in the magnitude of the splitting constants of amino proton and nitrogen can be expected.

In connection with these results, it may be interesting to mention the spectrum of the semiquinone ion with a betaine-like structure. The e.s.r. absorption of the semiquinone ion (V), formed by reduction of the compound  $C_{11}H_5O_3NCl_2$ , which can be prepared by the

condensation between chloranil and pyridine (20), has been examined. Unlike the naphthoquinone analogue (VI) (21) the structure of this product seems to be not yet well defined. The position of the substituents given in V are the most probable. The semiquinone ion shows only one absorption line and there is no structure due to the positively charged and trigonal-type nitrogen atom (Fig. 5).

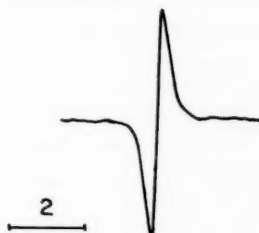
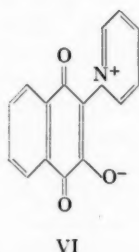
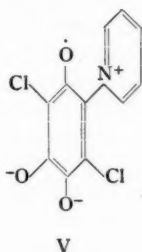


Fig. 5. First derivative of e.s.r. absorption spectrum of the semiquinone ion (V).



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# THE ELECTRON SPIN RESONANCE ABSORPTION SPECTRA OF SEMIQUINONE IONS

## PART III. FREE RADICAL SALTS OF QUINHYDRONES<sup>1</sup>

YOSHIO MATSUNAGA<sup>2</sup>

### ABSTRACT

Electron spin resonance absorption was observed in alkali salts of tetrachloro-*p*-benzoquinhydrone, *p*-biphenquinhydrone, and its tetrachloro and tetrabromo derivatives. The magnitude of *g*-value was found to be in the order of unsubstituted < chloro derivative < bromo derivative, and benzoquinhydrone salt < the corresponding *p*-biphenquinhydrone salt. The frequency of C—O stretching vibration was observed in the range 1525 to 1550 cm<sup>-1</sup>. Based on these frequencies the estimation of the parameters which are necessary for the molecular orbital treatment of semiquinone ions was attempted. A set of  $\alpha_0 = \alpha + (1/3 - 1/2)\beta$  and  $\beta_{CO} = \beta$  were derived. Independently values of  $\alpha_0 = \alpha + 2/3\beta$  and  $\beta_{CO} = \beta$  were estimated using the hyperfine structure of the electron spin resonance spectrum of the  $\alpha$ -naphthosemiquinone ion.

### INTRODUCTION

A number of unstable salts of quinhydrone have been described by organic chemists (1). It is well known that quinhydrone, which have no unpaired electron, dissociate into free radical ions in alkaline solution. Therefore, it seemed to be of interest to study the electronic structure of alkali salts of quinhydrone in the solid state. Electron spin resonance (e.s.r.) absorption has been detected in the quinhydrone adsorbed on barium hydroxide octahydrate (2). The highly colored reaction products of tetrahalogeno-*p*-benzoquinones with alkali iodides have been examined by the magnetic resonance method and found to be free radical salts (3). Here we wish to present the results of the e.s.r. and the infrared absorption measurements on sodium salts of *p*-biphenquinhydrone and its halogeno derivatives.

### EXPERIMENTAL

**Materials.**—Potassium salt of tetrachloro-*p*-benzoquinhydrone was prepared by the method of Torrey and Hunter (4). Chloranil was dissolved in cold, dry acetone and treated with crystals of potassium iodide. The grass green precipitate was filtered and washed with ether. According to Torrey and Hunter, the composition of the product is C<sub>6</sub>Cl<sub>4</sub>O<sub>2</sub>·C<sub>6</sub>Cl<sub>4</sub>(ONa)<sub>2</sub>. The sodium salt was also prepared by a similar method. Oxidation of biphenol with ferricyanide in alkaline medium gave sodium salt of biphenquinhydrone as described by Willstätter and Kalb (5). Biphenol was used in excess to avoid overoxidation. The blue product was quickly filtered and dried without washing. This salt decomposes quickly in contact with water. Tetrachloro-*p*-biphenol, which was obtained by chlorination of biphenol suspended in acetic acid (6), was dissolved in aqueous solution of sodium hydroxide and oxidized to sodium salt of quinhydrone using ferricyanide. The precipitate changes its color from violet to blue by washing with water. This free radical salt is so stable as to be prepared in the presence of a large excess of the oxidizing reagent. The dark blue salt of tetrabromo-*p*-biphenquinhydrone was prepared similarly (7). Bromination of biphenol was carried out as described by Magatti (6).

**Magnetic measurements.**—Electron spin resonance absorption was measured at room temperature at a frequency of 9 kMc/s. The *g*-value was estimated by comparison with

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diphenylpicrylhydrazyl (DPPH). The line width was taken as the distance in oersteds between the points of maximum slope.

*Optical measurements.*—Infrared spectrum was recorded using a Perkin-Elmer spectrometer model 21. The sample was examined in a potassium bromide disk.

### RESULTS AND DISCUSSION

All of our specimens showed e.s.r. absorption and we could conclude that alkali salts of quinhydrones consists of negatively charged semiquinone ions and alkali cations. The spin concentration in our specimens was found to be in the order of  $10^{21}$  to  $10^{23}$  spins per mole. The  $g$ -value, line width of e.s.r. absorption, and the frequency of C—O stretching vibration are presented in Table I. Our  $g$ -values for tetrachloro-*p*-benzoquinhydrone salts are in agreement with  $2.0044 \pm 0.0008$  for the sodium salt reported by Kainer, Bijl, and Rose-Innes (3). The infrared spectra of a number of ionic molecular compounds between quinones and aromatic diamines have been examined by Kainer and Otting (8). They have assigned the strong absorption band found in the region of 6.5 (ca.  $1540 \text{ cm}^{-1}$ ) to the C—O stretching vibration in tetrahalogeno-*p*-benzosemiquinone ions. Our results on much simpler compounds support their assignment.

TABLE I  
 $g$ -Value and line width of e.s.r. absorption and frequency of C—O stretching vibration  
in alkali salts of quinhydrones

	E.s.r. absorption		
	$g$ -Value	Line width in oersteds	C—O vibration in $\text{cm}^{-1}$
Na tetrachloro- <i>p</i> -benzoquinhydrone	$2.0051 \pm 0.0003$	6.7	$1530 \pm 10$
K tetrachloro- <i>p</i> -benzoquinhydrone	$2.0048 \pm 0.0003$	7	$1525 \pm 5$
Na <i>p</i> -biphenquinhydrone	$2.0044 \pm 0.0003$	5	$1550 \pm 5$
Na tetrachloro- <i>p</i> -biphenquinhydrone	$2.0064 \pm 0.0003$	2.2	$1540 \pm 5$
Na tetrabromo- <i>p</i> -biphenquinhydrone	$2.012 \pm 0.001$	1.5	$1530 \pm 5$

The magnitude of  $g$ -values of biphenquinhydrone salts was found to be in the following order:



The  $g$ -value for sodium salt of tetrabromo-*p*-benzoquinhydrone has been reported to be  $2.0068 \pm 0.001$  (3); therefore, the above order seems to be followed also by the series of benzoquinhydrone salts. The same tendency is found in the series of substituted DPPH and of substituted triarylammonium perchlorates (9). Consequently, we may conclude that substituted bromine atoms are more effective in enhancing spin-orbital coupling and in increasing the magnitude of  $g$ -value than substituted chlorine atoms regardless of the sign of charge on free radical molecules. However, it must be noted that the magnitude of  $g$ -value depends also on the size of semiquinone ions. Biphenquinhydrone salts give higher  $g$ -value than the corresponding benzoquinhydrone salts. These tendencies seem to be in sharp contrast to the results on aromatic hydrocarbon-iodine complexes (10). In the latter case, their  $g$ -values have been found to be close to that for free electron (2.0023) and the magnitude decreased with the increasing of the size of hydrocarbon molecule. In connection with the different behavior between these two kinds of halogens, it may be interesting to cite Wahler and Thon's observation that the magnitude of

g-value of diarylnitrogen oxide in solution shows a marked decrease by addition of complex-forming agent, *m*-dinitrobenzene and *s*-trinitrobenzene (11).

The hyperfine structure of the e.s.r. spectra of semiquinone ions in the dissolved state arises from the interaction between the magnetic moment of the unpaired electron and the magnetic moments of the protons in the molecule. Based on the spectra of *o*- and *p*-benzosemiquinone ions McConnell has suggested that the magnitude of ring proton splitting is approximately proportional to the density of the unpaired  $\pi$ -electron on the adjacent carbon atom (12). This approximation has been applied successfully to the case of aromatic hydrocarbon monopositive and mononegative ions (13, 14) and even to the case of DPPH (15). McConnell has used in his molecular orbital treatment of benzosemiquinone ions the following parameters without considering the effect of negative charge on the magnitude of coulomb integral for the oxygen atoms,  $\alpha_0 = \alpha + \beta$  and  $\beta_{CO} = \beta$  which were originally estimated for the oxygen atoms in neutral quinone molecules. It seems desirable to find a correct set of parameters for the application of this approximation to semiquinone ions with more complicated molecular structure. Therefore, we examined the C—O stretching vibration in the above-mentioned salts of quinhydrones and attempted to estimate the required parameters based on it.

Bonino and Scrocco (16) have suggested the use of the following relation between the mobile bond order ( $p_{CO}$ ) and the force constant of C=O bond ( $k$ ) for the estimation of stretching vibration frequency,

$$[1] \quad k = \xi p_{CO} + \sigma(1 - p_{CO}),$$

where  $\xi$  is the force constant for the "imaginary" double bond with  $p_{CO} = 1$ , and  $\sigma$  is that for C—O single bond. Although Berthier, Pullman, and Pontis (17) have presented a more refined equation considering the autopolarizability of the bond, we may use the above approximation ignoring the minor correction term. The values for the C=O bond in the formaldehyde molecule are used to estimate the magnitude of  $\xi$ , i.e.  $k = 13.45 \times 10^5$  dyne/cm (18) and  $p_{CO} = 0.958$  (17, 19), and we assume  $\sigma = 5 \times 10^5$  dyne/cm. The relation between the vibration frequency ( $\nu$ ) and the force constant estimated by equation [1] can be approximated by

$$[2] \quad \nu = 1744 (k/13.45 \times 10^5)^{1/2} \text{ cm}^{-1}$$

where  $1744 \text{ cm}^{-1}$  is the observed frequency for the C=O bond of the formaldehyde molecule (18).

TABLE II  
Calculated mobile bond orders, force constants, and stretching frequencies for the C—O bond in semiquinone ions

	$\alpha_0$	Mobile bond order, $p_{CO}$	Force constant $k \times 10^{-5}$ by eq. [1]	Frequency in $\text{cm}^{-1}$ by eq. [2]
<i>p</i> -Benzosemiquinone ion	$\alpha$	0.655	10.77	1561
	$\alpha + 1/2\beta$	0.609	10.36	1531
	$\alpha + \beta$	0.561	9.94	1499
<i>p</i> -Biphenosemiquinone ion	$\alpha$	0.672	10.91	1571
	$\alpha + 1/2\beta$	0.608	10.35	1530
	$\alpha + \beta$	0.537	9.73	1483



The calculated mobile bond order, force constant, and vibration frequency for benzo- and biphenyl-semiquinone ions are summarized in Table II. These results were obtained assuming  $\alpha_0 = \alpha + \beta_{CO} = \beta$ . The relation between the parameter and the vibration frequency  $\nu$  for the C—O bond in *p*-benzosemiquinone ion can be approximated by  $\nu = 1561 - 61\delta$  in  $\text{cm}^{-1}$ . The observed frequencies given in Table I suggest that the value of  $\delta$  in the present case is about one half. If we assume a similar linear relationship in the case of *p*-biphenylsemiquinone ion, the value of  $\delta$  will be estimated as one-third to one-half. These two estimations are in good agreement with each other.

The magnitude of parameters  $\delta$  can be estimated based on the hyperfine structure of e.s.r. spectrum.  $\alpha$ -Naphthylsemiquinone ion (Fig. 1) gives a spectrum of three quintets; therefore the density of unpaired electron on the aromatic carbon atoms 5 and 5' is practically equal to that on the carbon atoms 6 and 6' (see structural formula). If the square of the coefficient of  $2p$  function at the carbon atoms 5 and 6 are supposed to be equal to each other in the singly occupied molecular orbital, we obtain  $\delta = 2/3$  and the following densities of unpaired  $\pi$ -electron by the secular equations assuming  $\alpha_0 = \alpha + \beta$  and  $\beta_{CO} = \beta$ ; 0.225 on the oxygen atoms 1 and 1', 0.100 on the carbon atoms 2, 2', 3, and 3', and 0.025 on the carbon atoms 4, 4', 5, 5', 6, and 6'. If we apply the relation  $a_j = 34\rho_j$  given by McConnell for benzosemiquinone ions, where  $a_j$  is the ring proton splitting constant and  $\rho_j$  is the density of the unpaired  $\pi$ -electron on the adjacent carbon atom  $j$ , we may expect the splitting constants of 3.40 oersteds for the ring protons 2 and 2', and 0.85 oersted for the ring protons 5, 5', 6, and 6'. Although we cannot reproduce the observed pattern of spectrum using these constants, the estimated values are in good agreement with  $3.22 \pm 0.03$  oersteds and  $0.57 \pm 0.03$  oersteds given by Adams, Blois, and Sands (20).

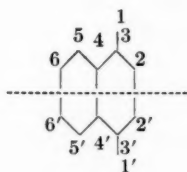


FIG. 1.

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# THE ELECTRIC MOMENTS OF SUPPOSEDLY SYMMETRICAL CYCLIC SUBSTANCES<sup>1</sup>

C. C. MEREDITH AND GEORGE F WRIGHT

## ABSTRACT

The distortion polarizations of polysubstituted benzenes and cyclobutanes which have been examined by the randomly oriented solid pellet technique seem to be lower but never higher than the electronic polarization values derived from bond refractions, and are considered to be more reliable than the latter. In almost all of the supposedly symmetrical substances which have been examined the total solute polarization always exceeds the measured distortion polarization and usually exceeds the calculated  $MR_D$ . These substances must then be polarized, although the moments which have been determined are not numerically reliable because of solvent effects. Whenever possible the temperature coefficients of these apparent moments have been determined and are usually but not always positive. From these temperature coefficients it is presumed that some substances, like naphthalene, are rigidly dipolar whereas others, like hexachlorobenzene, have activation states which are unsymmetrical and therefore contributory to the moment which actually is measured.

The graphic formula of a single molecule is patently a cursory description of a chemical substance, useful chiefly for illustrative and bibliotechnical communication. Nevertheless there seems to be a tendency to ascribe to the graphic formula a verity which it does not deserve. Especially is this the case when molecular symmetry is concerned. Indeed the simple diagram may become an unexcited state of reference in analysis of "loss" determinations such as those of absorption spectroscopy, or it may be used as the basis for trial structures during diffraction studies. There is some danger that the inadequate graphic formula thus becomes "built into" the physical interpretation.

Although a reactance determination, of which dielectric constant is an example, has the obvious disadvantage of an integrated, non-detailed result in which the entire system participates it does not require the same degree of preconception that is common to some other physical methods. No irreversible energy transfer occurs, so that the measurement is that of the actual system if sufficiently weak electromagnetic fields are applied. If environmental influences can be evaluated, say by variation of solvent, temperature, and concentration, the modulated value of electrical polarization sets a definition to which the molecular construct of the substance must conform.

This definition is especially applicable to substances for which the graphic formula would predict, for reasons of symmetry, a zero dipole moment. Several examples in which the inadequacy of the ordinary graphical construct becomes apparent, have recently been reported (1-4).

In the present report this list has been extended to include aromatic hydrocarbons with aliphatic and halogeno substituents. These substances would not be expected to display any orientation polarization if the frequently quoted symmetries and the graphic formulae specifying them were valid.

In some instances zero moments have been assigned heretofore to substances showing low total polarizations,  $P_T$ , because the intuitive decision from the graphic formula was at least as meaningful as the ostensible orientation polarization remaining after subtraction from  $P_T$  of a questionably calculated distortion polarization ( $P_{e+a}$ ). Little accuracy can be claimed for the usual (2-5% of  $P_E$ ) assignment of atom polarization. However, now we are aided in this respect by the actual determination of the entire distortion

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TABLE I  
 Distortion polarizations and molecular refractions

Substance	Density	Dielectric constant	$P_{e+s}$ , cc	Vogel $C_{ar}-C_{ar}$	Vogel $C=C + C-C$ , cc	Eisenlohr, cc
Naphthalene	1.156	2.729	40.5	43.0	42.0	41.6
Anthracene	1.243	3.022	57.7	59.7	57.6	57.0
Phenanthrene	1.176	2.852	57.8	59.7	57.6	57.0
Chrysene	1.284	3.045	72.0	76.6	72.6	72.3
Pyrene	1.280	2.921	61.6	67.8	64.4	61.6
Hexahelicene	1.249	2.850	100.2	110.2	104.3	103.0
Coronene	1.378	3.192	91.2	100.8	93.5	92.0
Fluorene	1.209	2.821	51.9	52.9	53.4	52.8
Durene	1.036	2.340	39.9	44.8	45.0	44.8
Hexamethylbenzene	1.043	2.366	48.6	54.1	54.3	54.0
Acenaphthene	1.204	2.738	46.9	50.2	47.3	48.7
<i>o</i> -Diphenylbenzene	1.173	2.660	69.8	74.4	75.2	74.5
<i>p</i> -Diphenylbenzene	1.231	2.888	72.2	74.4	75.2	74.5
1,4-Di- <i>tert</i> -butylbenzene	0.950	2.281	59.8	63.4	63.6	63.2
Azulene	1.275	3.078	41.1	43.0	42.0	41.6
Ferrocene	1.537	2.844	46.2	43.6 <sup>a</sup>	41.2 <sup>a</sup>	41.1 <sup>a</sup>
1,2,3,4-Tetraphenyl-cyclobutane, m.p. 163°	1.162	2.626	109.0	121.3 <sup>b</sup>	116.2 <sup>b</sup>	114.8
Same, m.p. 149.7°	1.159	2.623	109.2	121.3	116.2	114.8
Hexachlorobenzene	2.045	2.833	53.0	55.2	55.5	55.5
1,2,4,5-Tetrachlorobenzene	1.732	2.586	43.1	45.5	45.8	45.8
1,4-Dimethyl-2,3,5,6-tetrachlorobenzene	1.703	2.738	50.9	54.8	55.1	55.0
Azobenzene	1.205	2.743	55.5	55.3	55.8	
<i>trans</i> -Stilbene	1.144	2.7307	59.1	59.6	60.3	59.2
1,4-Diphenylbutadiene	1.121	2.850	70.2	67.1	67.8	67.3
1,6-Diphenylhexatriene	1.075	2.695	78.0	74.6	75.4	76.6
2,5-Diphenyldithiene	1.363	3.038	79.6	80.4	81.0	81.1
Methyleneanthrone	1.331	3.120	64.1	61.7	62.2	61.6
Beta-carotene	1.141	2.940	184.8		174.7	177.4
1,2-Diiodotetrafluorobenzene	2.966	2.719	49.4	50.7	50.9	49.8
1,2,4,5-Tetrachlorobenzene	1.732	2.586	43.1	45.5	45.7	45.8
1,4-bis-Chloromethylbenzene	1.432	2.915	47.6	45.2	45.4	45.3
1,4-bis-Trichloromethylbenzene	1.743	2.649	63.6	64.5	64.8	64.8
Tetraphenylethylene	1.148	2.466	95.7	107.3	108.4	107.3

<sup>a</sup>The calculated refractions do not include iron II for which a value of 5.0 cc may be estimated.

<sup>b</sup>If Vogel's value for the cyclobutane C—C bond refraction had been used (1.37 cc) instead of the usual C—C value (1.29 cc) these additive refractions would be higher than is recorded.

<sup>c</sup>Kindly furnished by H. J. Matsuguma, Picatinny Arsenal, Dover, N.J., m.p. 50.5–51.8°. Prepared by W. J. Pummer, R. E. Florin, and L. A. Wall. J. Research Natl. Bur. Standards, **62**, 113 (1959).

polarization from the dielectric constant of the randomly oriented, highly compressed solid in which no orientation polarization should be detectable (1). In general the results have conformed with expectations. However in some instances apparent abnormal atom polarizations, previously assigned in order to conciliate an observed total polarization with an intuitively defined zero moment, have been found to be non-existent (1, 3, 4). On the other hand some hitherto unsuspected atom polarizations have been discovered (2).

Although the measured distortion polarization ought to be and customarily is higher than the molecular refraction (because the latter does not include atom polarization) we have earlier encountered an exception in diphenylmercury (4). Since we have suspected that this behavior is due to the phenyl groups, and our present candidates are aromatic, we have examined a series of this type of hydrocarbon in respect of distortion polarization measured in pellets at 23°. The results are shown in Table I together with molecular refractions calculated in three ways.

In the column "Vogel  $C_{ar}-C_{ar}$ " (5) the value of 2.69 cc has been used for aromatic ring bonds. In the following column "Vogel  $C=C+C-C$ ," 4.17 cc and 1.30 cc respectively are used for aromatic rings. Finally in the last column are the additions of atom refractions according to Eisenlohr (6), all being values for the  $Na_D$  frequency.

The three additive refraction calculations are not interconsistent. Of present interest is the comparison of these calculated molecular refractions with our measured distortion polarizations ( $P_{e+a}$ ). First it may be seen that  $P_{e+a}$  for simple aromatic hydrocarbons is consistently lower than  $MR_D$  from Vogel's  $C_{ar}-C_{ar}$  bond value (perhaps because he derived the value from the most aromatic of all hydrocarbons, benzene) and to a lesser extent lower than  $MR_D$  from Vogel's  $C=C+C-C$  values. On the other hand  $MR_D$  from Eisenlohr's values agrees with our measured  $P_{e+a}$ . But this latter agreement must be fortuitous because all  $MR_D$  values are larger than measured  $P_{e+a}$  when substituents (either alkyl, halogen, or even phenyl) are considered.

In several instances there is good agreement between  $MR_D$  calculated and  $P_{e+a}$  observed, for example, azobenzene and stilbene. The case of stilbene is especially propitious because the refractive indices of the crystals have already been measured carefully at a series of wavelengths (7) in the visible region. If the mean of the indices along the three principal axes  $(\eta_\alpha + \eta_\beta + \eta_\gamma)/3$ , is calculated for each wavelength the linear distribution of these mean values with respect to wavelength justifies the application of the Cauchy dispersion equation (8) for calculation of the refractive index at infinite wavelength,

$$n_\infty = \frac{(3650)^2 \cdot 10^6 (1.931) - (6908)^2 \cdot 10^6 (1.739)}{10^6 \cdot (3650)^2 - (6908)^2 \cdot 10^6} = 1.664,$$

whence the  $MR_\infty$  may be calculated

$$\frac{(1.664)^2 - 1}{(1.664)^2 + 2} \cdot \frac{180}{1.144} = P_e = 58.5 \text{ cc.}$$

This electronic polarization is about 1% lower than our measured  $P_{e+a}$ , as might be expected for a normal contribution of atom polarization. On the other hand  $MR_D$  calculated according to Vogel is 1-3% higher than our measured  $P_{e+a}$ . It would seem that Vogel's bond refractions derived at short wavelength thus are not closely applicable to distortion polarizations in the radiofrequency range.

Even the Eisenlohr value of 59.2 cc for  $MR_D$  of stilbene may be too high, despite apparent agreement with  $P_{e+a}$ , if an exaltation not calculated into  $MR_D$  actually is included in the distortion polarization which we have measured. The existence of this exaltation is not improbable if one considers the measured distortion polarizations of *trans-trans*-1,4-diphenylbutadiene and *trans-trans-trans*-diphenylhexatriene, which are appreciably higher than the  $MR_D$  values for which no exaltation has been included (Table I). These observations of exaltation in the radiofrequency range seem to be reliable since other substances like  $\beta$ -carotene and, perhaps, methyleneanthrone also give exalted values (Table I). On the other hand the measurement  $P_{e+a}$  for the highly degenerate tetraphenylethylene is quite low.

Further examinations of the polarizations shown in Table I disclose many discrepancies between observed and calculated values. The measured distortion polarizations of the polynuclear hydrocarbon are in reasonable agreement with Eisenlohr calculations of  $MR_D$ , but both are markedly lower (particularly note coronene) than Vogel's calculated  $MR_D$ , especially when Vogel's  $C_{ar}-C_{ar}$  value is used. On the other hand the Eisenlohr  $MR_D$

seems to be at least as much higher (and sometimes more so) than the measured  $P_{\text{e}+\text{s}}$  as is the Vogel value when the aromatic nucleus is substituted by methyl, chloro, or phenyl groups. If experimental errors (such as preferential orientation or dimensional non-uniformity of the compressed wafer) are avoided the measured distortion polarization ought to be the most reliable value. Likewise the lowest value ought to be the most realistic because errors due to electrical conduction or dielectric loss tend to raise the apparent dielectric constant. Therefore one may fairly question the calculated electronic polarization for substances in which aromatic linkages exist.

In point of fact the vagaries of calculated distortion polarization have been significant in the consideration of total polarizations when a certain orthodoxy would decree zero moment for the substance under examination. The polarization of naphthalene is a typical instance. The concept of resonance, supported by careful X-ray diffraction studies of crystalline naphthalene (9), and despite some minor discrepancies (10), seems to have firmly established the planar symmetry of this substance. However, in benzene at 20° the total solute polarization ( $P_T$ ) was found to be 45.1 cc (11). In heptane at 20° the  $P_T$  must have been found to be 45.4 cc (12) because a tentative moment of 0.34 Debye (D) was calculated. But this value was abandoned in favor of  $\mu = 0$  by deduction of 10 to 15% as atom polarization. The lowest total polarization reported in the literature is 43.3 cc but the author (13) was trying to avoid a previous error. Perhaps he overcorrected.

In all of these instances there seems to have been an effort to force the dipole moment of naphthalene to zero. This tendency is understandable in view of the orthodox expectancy from X-ray diffraction studies versus a distrust of the electrical measurement. This distrust is not unreasonable when low orientation polarizations are involved because a consistent error (say residual cell capacitance and/or inductance in leads) can easily lead to a spurious value of polarization.

Of course techniques have improved during the past 25 years. Among these improvements are those in our own apparatus in which inductance and capacitance errors have been avoided in large part by rigid location of the test capacitance as close as possible to the principal parts of the resonant circuit. We are accustomed to test the effectiveness of this and other precautions by polarization measurements of carbon tetrachloride in benzene and of benzene in carbon tetrachloride. Examples of such tests are shown in Table II.

It may be seen that neither benzene nor carbon tetrachloride shows an appreciable orientation polarization.

TABLE II  
Electrical polarizations of carbon tetrachloride, benzene, and naphthalene

Solute	Solvent	Temp., °C	Dielectric constant of solvent		Spec. vol. of solvent		$\delta\epsilon/\delta\omega$	$\delta V/\delta\omega$	$P_T$ , cc	$MR_D$ , cc	$P_s$ , cc	$\mu$ , D
			Deter- mined	Extra- polated	Deter- mined	Extra- polated						
$C_6H_6$	Dioxane	20	2.2179	2.2175	0.96743	0.96740	0.04	0.168	26.1	26.2	-0.1	0
$C_6H_6$	$CCl_4$	20	2.2409	2.2410	0.62707	0.62705	0.07	0.500	26.1	26.2	-0.1	0
$CCl_4$	$C_6H_6$	20	2.2846	2.2846	1.13769	1.13770	-0.09	0.500	26.9	26.2	0.7	0.05
$C_{10}H_8$	$C_6H_6$	20	2.2846	2.2845	1.1377	1.13790	0.43	0.195	46.6	40.5 <sup>a</sup>	5.0-6.1	0.49-0.55
$C_{10}H_8$	$C_6H_6$	40	2.2405	2.2412	1.1673	1.16750	0.31	0.130	46.4	41.6	4.8-5.9	0.49-0.54
$C_{10}H_8$	$CCl_4$	20	2.2378	2.2373	0.6270	0.6270	-0.35	0.129	43.1		1.5-2.6	0.3
$C_{10}H_8$	$C_6H_{12}$	20	2.0243	2.0245	1.2787	1.2787	0.28	0.158	43.2		1.6-2.7	0.3

<sup>a</sup>Directly determined distortion polarization.



On the other hand this table shows that for naphthalene in benzene a significant orientation polarization (40.5 cc) or of the Eisenlohr  $MR_D$  (41.6 cc) from the observed total polarization. The latter value (46.5 cc) is quite comparable with those obtained by Parts and by Briegleb, but unlike the latter worker we choose to assign a moment of 0.49–0.54 D to naphthalene in benzene. The apparent moments in carbon tetrachloride and cyclohexane are lower but still significant.

Although this assignment may seem to be anomalous in view of X-ray diffraction studies it is not unexpected on the basis of chemical evidence. Since both rings cannot be complemented by pi sextets some other charge distribution must be prevalent. The behavior of naphthalene upon ozonization and addition of halogen strongly indicates (14) that the electronic distribution tends toward 6:4. That is to say, one ring tends to be fully aromatic and the other to be conjugated aliphatic in behavior. The substance may then be classified as mesoionic in its degeneracy and this resonance state is justified by the independence of dipole moment with respect to temperature (Table II). The mesoionic concept seems not to be contradicted by the normal distortion polarization of naphthalene because azulene, which is certainly mesoionic, does not exhibit any abnormality in the measured  $P_{e+a}$ .

The examples which are elaborated above provide some justification for the use of measured distortion polarizations in moment studies, but there are many unexplained differences between  $P_{e+a}$  and  $MR_D$  to be found in Table I. In the search for error there are several possibilities. In the experimental determination low values are to be expected if the compressed wafer which we measure is not at maximum density. However, this error may be detected either by nonlinearity of the plot of thickness versus apparent dielectric constant, or else by comparison of the density of individual crystal fragments with the density of the wafers. Another error, that of preferred orientation of crystal fragments (say, of plate-like crystals), may be avoided simply by our practice of reforming ground wafers.

Turning from the practical to the theoretical aspects, the application of polarizations determined in the crystalline state to systems in which lattice forces are not present might be thought to introduce a damping error. But in measurements of dielectric constant which have been made in the vicinity of the melting point (15, p. 134) there seems to be no evidence of a significant lattice restriction on distortion polarization. Moreover, the concept that atom polarization is a reactive compensation of electronic charge deformation would imply for a restriction of atom polarization in crystals a corresponding difference in refractive index between liquids and solids. In general such differences are not observed (16). In particular the comparison of molar refractions calculated from  $(\eta_\alpha + \eta_\beta + \eta_\gamma)/3$  (which is essentially the same as when calculated from  $\sqrt[3]{\eta_\alpha \cdot \eta_\beta \cdot \eta_\gamma}$ ) with the  $MR_D$  calculated from group refractions for stilbene in the present publication and for N,N'-dinitropiperazine in an earlier one (17) show that the electronic polarization is not altered appreciably by change of state. Therefore from both the practical and theoretical aspects the direct measurements of distortion polarization would seem to be reliable.

On the other hand errors in molecular refraction are less easy to define. When solids are involved the calculation is usually indirect, involving generalized atom or bond refractions. The summation of additive refractions has been shown in Table I to be capricious. Moreover, the extrapolation from optical to radio frequencies is unreliable unless the electromagnetic losses (spectral absorption or loss tangent) are known. Unfortunately instruments are not yet available to cover this entire spectral range. Even if these faults of evaluation could be overcome, the actual atom polarization would only be estimated

as an arbitrary increment to equate electronic to the entire distortion polarization. Indeed the only reliable method (except for the direct measurement of pelleted solids) is the measurement of total polarization for a substance the dipole moment of which is zero. In this instance total and distortion polarization are equal. However, it is shown below that substances of zero dipole moment are uncommon.

#### POLARIZATIONS OF SUBSTANCES TO WHICH CENTROSYMMETRY OFTEN IS ASCRIBED

Some of the substances described in Table III have been studied because considerations of the graphic formulae (sometimes fortified by X-ray diffraction) would indicate absence of electric moment. Of course these graphic formulae depict unperturbed molecules isolated in space, a circumstance never realized during ordinary chemical reactions. Nevertheless if the activated states and the effects of environment were grossly symmetrical the moments ought to be zero. It may be seen in Table III that this expectation is not realized.

In the case of hexamethylbenzene the answer is dependent on the choice of a distortion polarization value. The calculated electronic polarization happens to be about the same according to either Vogel or Eisenlohr. We suspect by perusal of Table I that this agreement involves a compensation of error. However, the value is so close to that of the total polarization at 20° or 40° that the moment might be specified as zero. On the other hand the measured distortion polarization is sufficiently lower than  $P_T$  that a moment of 0.52 D may be assigned. This apparent moment is not sufficiently augmented (0.56 D) at 40° to justify an assignment more definite than 0 to 0.5 D for hexamethylbenzene, depending upon whether measured  $P_{e+a}$  or calculated  $MR_D$  is used in the calculation.

The situation is somewhat clearer for 1,4-di-*tert*-butylbenzene because both the calculated ( $P_e$ ) and observed ( $P_{e+a}$ ) distortion polarizations are less than the total polarization. Since  $P_{e+a}$  is lower than  $MR_D$  (calculated) there is no justification for inclusion of an abnormal atom polarization with the latter value. The calculated moment of 0.58 D (or 0.4 D in respect of  $MR_D$ ) in benzene at 20° is augmented to 0.64 D at 40°. This difference (which is beyond our estimated error of  $\pm 0.01$  D) would indicate that the *tert*-butyl groups comprise an opposed quadrupole in absence of thermal agitation. Therefore at some temperature much below those which must be chosen if benzene is the solvent a zero moment should be observed.

Similarly the orientation polarization of 1,4-diphenylbenzene may be attributed to thermal agitation. The measured  $P_{e+a}$  and calculated  $MR_D$  differ by about 3%, but they are both lower than  $P_T$  in benzene at 20° so a moment of 0.60 to 0.51 D may be calculated, which is 0.73–0.64 D at 40°.

It is evident that substances like these of ostensible zero moment cannot be used for standardization of electrical polarization equipment if they display orientation polarizations. In this connection it is pertinent to review the polarization studies of 1,4-dichlorobenzene which is sometimes considered to be such a standard substance. Thus Briegleb (12) must have observed a total polarization at 20° in heptane of 40.4 cc and an electronic polarization of 36.1 cc, yet he discards the predicted moment of 0.45 D, preferring a hypothetical atom polarization to contradiction of an intuitive expectation of static symmetry. Unfortunately for purposes of clarification we cannot contradict Briegleb by measurement of the dielectric constant of 1,4-dichlorobenzene because its low melting point prevents the preparation of satisfactory pellets. However, we obtain polarization values in benzene and in dioxane from which moments of 0.43 D and 0.33 D, respectively,

TABLE III  
 Dipole moments of hydrocarbons and their halogenated derivatives

Substance	Solvent	Temp., °C	$\delta e/\delta u$	$\delta V/\delta u$	$P_T$	$P_{e+u}$	$R_D$ calc.	$\mu$ from $P_{e+u}$	$\mu$ from $R_D$	Comments
Hexamethylbenzene	Benzene	20	0.060	0.057	54.3	48.6	54.1	0.52	0	
		40	0.051	0.044	54.8			0.56		
1,4-Di- <i>tert</i> -butylbenzene	Benzene	20	0.030	0.025	67.3	60.2	63.4	0.58	0.4	
		40	0.017	0.009	68.3			0.64		
1,4-Diphenylbenzene	Benzene	20	0.43	0.247	79.8	72.2	74.6	0.60	0.51	
		40	0.51	0.280	82.5			0.73	0.64	
Hexahelicene	Benzene	20	0.56	0.363	110.4	100.2	105	0.70	0.4	
1- $\downarrow$ -2- $\downarrow$ -3 $\uparrow$ -4 $\uparrow$ -	Benzene	20			113			0.44	0 <sup>a</sup>	<sup>a</sup> Latter values actually calculated as if $R_D$ was 113 cc
Tetraphenyl-	Benzene	40			126			0.93	0.82	
cyclobutane,	Dioxane	20			126	109	116	0.90	0.80	
m.p. 163°	Dioxane	40			151			1.46	1.38	
1- $\downarrow$ -2,3,4- $\uparrow$ -	Benzene	20			119.4			0.69	0.55 <sup>a</sup>	
Tetraphenylcyclo-	Benzene	40			147.6			1.41	1.32	
butane, m.p. 149°	Dioxane	20			142.6	109	116	1.27	1.16	
	Dioxane	40			182.0			1.92	1.87	
$\alpha$ -Methylstyrene	Benzene	20	0.80	0.055	55.9		39.4		0.80	
<i>trans</i> -Propenylbenzene	Benzene	20	0.52	0.034	50.5		40.7		0.68	
<i>cis</i> -Propenylbenzene	Benzene	20	0.57	0.048	51.1				0.70	
		40	0.57	0.088	51.4		40.8		0.69	
2-Methyl-1-phenyl-1-										
propene	Benzene	20	0.63	0.050	63.8		49.4		0.83	
1,4-Dichlorobenzene	Dioxane	20	0.23	0.195	38.4		36.0		0.33	<sup>b</sup> $R_D$ gives $R_D$ of 36.7
							36.7 <sup>b</sup>		0.28	
	Benzene	20	0.18	0.353	39.5		36.0		0.41	
	Benzene	30	0.14	0.336	39.4		36.0		0.41	
Hexachlorobenzene		20	0.23	0.58	59.8	53.0	55.5	0.54		<sup>c</sup> Determinations made with temperature-variant apparatus
		30	0.33	0.60	64.3			0.72		
		30 <sup>c</sup>	0.35	0.599	65.7			0.76		
	Benzene	35	0.37	0.58	68.8			0.80		
		40 <sup>c</sup>	0.34	0.600	68.4			0.86		
		60 <sup>c</sup>	0.38	0.600	70.3			0.95		
	CCl <sub>4</sub>	20	0.28	0.071	54.7			0.21		
		30	0.45	0.092	58.7			0.50		
Hexafluorobenzene	Cyclohexane	20	0.09	0.605	36.2		26.5		0.67	
		30	0.10	0.49	38.9		26.5		0.81	<sup>d</sup> $\pi_D^{20} = 1.3760$ $d_4^{20} = 1.612$
	Benzene	40	0.10	0.49	40.2				0.83	
		60	0.10	0.49	40.9				0.88	
		20	1.16	0.768	131.4				1.96	
1,2-Diiodotetra-	Benzene	30	1.065	0.794	123.6	49.4	50.4		1.89	
fluorobenzene		40	0.96	0.802	119.2				-1.86	
1,4-Dimethyl-2,3,5,6-		20	0.16	0.370	63.4	50.9	55.0	0.77	0.63	
tetrachlorobenzene	Benzene	30	0.40	0.476	67.5			0.90	0.78	
		40	0.52					1.04	0.95	
1,2,4,5-Tetrachloro-		20	0.35	0.51	54.2	43.1	45.5	0.72	0.64	
benzene	Benzene	30	0.34	0.52	54.2			0.73	0.65	
		40	0.33	0.53	54.0			0.74	0.66	
1,4-Diiodotetra-										
fluorobenzene	Benzene	30	0.12	0.80	50.8	49.4	50.4	0.14	0	
1,2,3,4-Tetra-	Benzene	20	0.412	0.36	150.0		25.1		2.43	
fluorobenzene		30	0.392	0.39	145.6				2.41	
Tetraphenylethylene	Benzene	40	0.392	0.248	114.7	95.1	107.3	0.99	0.61	
	Benzene	20	0.03	0.179	97.3	95.1	107.3	0.33	-0.69	Absurd
	Dioxane	20	0.462	0.101	107.5	95.1	107.3	0.77	0	

may be calculated after subtraction of Briegleb's distortion polarization value. This solvent effect would not have been observed if an electrical dipole were absent. Therefore we see no reason to attribute a zero moment to *p*-dichlorobenzene at ordinary temperature nor to consider it as a reference standard, especially since in Table I analogous substances do not show abnormal distortion polarizations. Despite expectations from other studies

(18) the four polyhalogenobenzenes listed in the table all have  $P_{e+a}$  values which are about 4% lower than the calculated  $MR_D$  values.

The high group moments which may be anticipated in these halogenobenzenes makes them of especial interest with respect to studies of molecular symmetry. Among these substances hexachlorobenzene has been examined most completely by other physical methods. Single crystal X-ray diffraction studies show it to be planar (19) although a modern study might alter this opinion, especially in respect of the carbon atoms. Actually it is somewhat surprising that a centrosymmetrical molecule should exist in the polymorphic forms (20) that have been reported for this substance. At any rate when hexachlorobenzene is freed from its crystal lattice the chlorine atoms no longer remain coplanar. A displacement from planarity of about  $25^\circ$  is claimed on the basis of quadrupole moment (21). Indeed displacement is not even symmetrically disposed according to electron diffraction studies (22) which attribute this asymmetry to out-of-phase bending of the carbon-chlorine linkages.

Not only is this asymmetry indicated by our electrical polarization studies, but also the data of Table III show that the moment of hexachlorobenzene in benzene increases from 0.54 D to 0.95 D when the temperature is raised from  $20^\circ$  to  $60^\circ$ . Of course the absolute values of moment are in doubt. Quantitative assignments are precluded because of the disparity between calculated and observed distortion polarizations. Also (Table III) the solvent seems to be involved in the polarization because the apparent moment is smaller (0.2 D) in carbon tetrachloride at  $20^\circ$  than it is in benzene. Nevertheless the moment in carbon tetrachloride seems to be real, because it is augmented to 0.5 D at  $30^\circ$ . But also it cannot be an absolute value if it is temperature-dependent.

Although the lesser moment in carbon tetrachloride may be expected in view of the lesser polarizability of this medium, still one is not justified to specify the observed moment value as absolute. It is true that a substance like iodine displays no orientation in cyclohexane (23), and probably would not do so in carbon tetrachloride. In benzene, on the other hand, a moment is observed which must be due to mutual polarization of solvent and solute (iodine) either of which alone has no dipole moment. But when a solute (like hexachlorobenzene) is polar, at least in activated states, it may be expected to distort and therefore polarize substances like carbon tetrachloride which bound the solvent cavity in which it exists. In this sense the absolute polarity of a substance cannot be defined if it has neighbors. *But the existence of polarity can be defined.* Perhaps solvents like benzene and dioxane should be considered to be useful in enhancement of otherwise meager moments, at least until the time that more precise methods than now are known become available for measurement of electrical polarization.

Despite this limitation on the quantitative significance of the polarization of hexachlorobenzene it seems to be undeniable that this polarization shows it to be a nonplanar substance, the asymmetry of which increases with rising temperature. In order to understand this situation other halogenobenzenes have been examined. The first of these, 1,2,4,5-tetrachlorobenzene, apparently has a moment in benzene at  $20^\circ$  which is larger (Table II) than that of hexachlorobenzene. However, the augmentation of this moment with rising temperature is so slight that it is almost within experimental error. By contrast when methyl groups occupy the hydrogen positions in the tetrachlorobenzene, as in 1,4-dimethyl-2,3,5,6-tetrachlorobenzene, the moment in benzene at  $20^\circ$  is only slightly higher than in absence of these methyl groups. However, this moment is markedly augmented by increasing temperature (see Table III). It would seem that while steric obstruction (minimal in 1,2,4,5-tetrachlorobenzene) is not significantly responsible for

the inherent moments, it is largely responsible for the temperature-induced polarizability.

Polysubstitution of fluorine instead of chlorine on the benzene ring ought to reduce the steric obstruction, and indeed this expectation is borne out in the polarizability of the hexafluorobenzene kindly supplied to us by Dr. Wall of N. B. S. (24).

As was observed for hexachlorobenzene the apparent moment of the fluoro analogue is lower in cyclohexane than it is in benzene which is ostensibly more polarizable. However, the apparent moments for hexafluorobenzene in either solvent at 20° are higher (Table II) than the comparable values for the hexachloro analogue. This result would not be expected, if the moments were due to static nonplanarity, in view of the evidence (15, p. 253) that the group moment (1.46 D) for C—F is lower than that of C—Cl (1.58). On the other hand the result could be due to a dynamic nonplanarity in activated states. The difference in apparent moment is not great; indeed if one were to choose the admittedly improbable state of activation involving all six halogen atoms on one side of an assumed planar hexagon of carbon atoms the apparent moment would be accounted for by an angular deviation of 3° for the chlorine atoms and 5° for the fluorine atoms. Among the complexity of possible conformations of activation it is possible for the resultant moment of hexafluorobenzene to exceed that of hexachlorobenzene, especially since the lower force constant of the C—F bond would allow greater amplitude of deformation.

Of interest in relation to this concept of moment contributions from such a dynamic "structure" is the observation that the apparent moment of hexafluorobenzene increases by only 0.07 D over a temperature range of 40°. By contrast the apparent moment of hexachlorobenzene (although it is lower than that of hexafluorobenzene at 20° in benzene) increases by 0.41 D over the same range of temperature. This difference might be ascribed to a higher activation energy for hexachlorobenzene (due largely to steric obstruction) which is observed as a greater temperature coefficient for the dipole moment.

This interpretation is based upon the assumption that the activated states are appreciably unsymmetrical and that this asymmetry is accentuated when the activated state tends to be more sterically hindered than the base state. It is of interest to examine the behavior of a substance which undoubtedly is hindered in the base state. This condition prevails in the 1,2-diiodotetrafluorobenzene (25), which we have obtained by courtesy of Dr. Matsuguma at Picatinny Arsenal.

If this substance were entirely coplanar one would expect the moment to be the arithmetic difference between the moments of 1,2-difluorobenzene (2.38 D in benzene at 22°) (26) and of 1,2-diiodobenzene (1.70 D in benzene at 23°) (27). Instead of the expected 0.68 D the apparent moment of 1,2-diiodotetrafluorobenzene in benzene at 20° has been found to be 1.96 D.

Of course an abnormality for this compound is not entirely unexpected since the observed moment for 1,2-diiodobenzene is somewhat lower than the calculated (ref. 15, p. 332) value, 2.25 D. Presumably this diminution may be attributed to steric repulsion of the iodine atoms so that they are spread apart in a planar structure, or else oppositely forced above and below a plane.

It is evident that these deformations are not applicable to the structure of 1,2-diiodotetrafluorobenzene. The high moment would indicate the presence of contributing conformations where fluorine as well as iodine is forced asymmetrically from the plane of carbon atoms assumed to exist in these substituted benzenes. Of course the assumption of ring planarity is arbitrary, but it allows a simple description of conformation in which fluorine-carbon moments are supporting rather than detracting from iodine carbon moments.



By contrast the observed moment of 1,4-diiodotetrafluorobenzene, in which obstruction may be expected to be minimal, is very low (0.14 D in benzene at 30°), indicating cancellation of opposing group moments. In like manner the 1,4-fluorine atoms in 1,2,3,4-tetrafluorobenzene must be compensatory because the observed moment of this substance (2.43 D) is very close to that of 1,2-difluorobenzene. The absence of obstruction which is indicated by this agreement is further supported by the virtual invariance of moment in benzene at 20° and 30° (2.43 vs. 2.41 D, Table III).

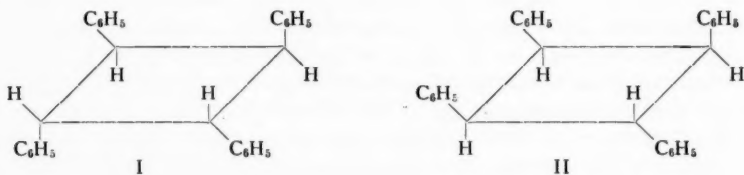
It may be seen from these examples that the effect of iodine atoms vicinally located on a benzene ring in which fluorine atoms prevent lateral spacing is profound. This is the circumstance in 1,2-diiodotetrafluorobenzene with its abnormally high apparent moment. It might be expected that when obstruction is sufficiently great it cannot become greater but must necessarily be less in activated states.

It may then be significant that the apparent moment of 1,2-diiodotetrafluorobenzene, alone among the moments of substances under consideration in this report, decreases slightly but significantly (1.96 to 1.84 D from 20° to 40°) with increasing temperature. The behavior is remindful of certain sterically hindered diastereomers, the moments of which have been studied recently with respect to temperature (28).

#### THE TETRAPHENYLCYCLOBUTANES

Several of the diastereomers of tetraphenylcyclobutane will now be discussed separately from the foregoing items of Table III because of the rigidity imposed by the cyclobutane ring.

The isomers are 1-↓-2-↓-3-↑-4-↑-tetraphenylcyclobutane, I, and 1-↓-2,3,4-↑-tetraphenylcyclobutane according to Morton, Bright, and Flood, who kindly loaned them to us. They specified these structures on the basis of nuclear magnetic resonance studies (29).



These workers obtained II (m.p. 149.7°) together with stilbene from the reaction of benzyl chloride with potassium amide in liquid ammonia. The preparation of I (m.p. 163°) had been accomplished by Fulton (30) when he irradiated stilbene and/or stilbamine with ultraviolet light. Fulton also obtained in trace amounts an isomer melting at 149°. However, this isomer is not identical with II, at least according to comparison of the X-ray pattern of II with that of a sample of Fulton's isomer, kindly furnished to us by Professor Dunitz, University of Zürich. Insufficient material was in hand to determine whether the difference was due to diastereoisomerism or polymorphism. Our studies have been made with the proved isomers I and II.

Actually the configuration of I was demonstrated by Professor Dunitz by a thorough single crystal X-ray study (31). However, he found that the isomer I was not conformationally symmetrical. Not only were abnormalities of bond shortening at C-phenyl observed, but also it appeared that the phenyl rings were not axially disposed with respect to these bonds; deviations up to 7° were suggested.



In this X-ray diffraction study Dunitz did not suggest any nonplanarity of the cyclobutane ring although he did report that the bond lengths differed. Later he and others presented evidence from studies of various cyclobutanes (including electron diffraction and infrared absorption) which indicate a dihedral angle in the cyclobutane ring, which may be as low as  $162^\circ$ . It is of interest that a calculation of the dipole moment of tetramethylcyclobutanedione-1,3, assuming that carbonyl moments of 2.5 D are inclined axially at  $162^\circ$ , gives the same resultant (0.8 D) which was obtained from the measured electrical polarization (3). It is against this background that we have studied the electrical polarizations of the tetraphenylcyclobutanes, I and II.

This study has brought forth several apparent anomalies. Firstly a measurement of the dielectric constant of the randomly oriented compressed solid isomers I and II gives distortion polarization ( $P_{e+a}$ ) values (109 cc, Table I) which are somewhat below the electronic polarization calculated from Vogel's and Eisenlohr's generalized bond refractions (32, 33) (121.3–114.8 cc). The measured value of 109 cc also is lower than that which may be calculated indirectly (116.5 cc) from the molecular refraction of cyclobutanecarboxylic ester (34).

In Table III it may be seen that the total polarization of isomer I in benzene at  $20^\circ$  is 113 cc. Since all of the values for  $MR_D$  are higher than 113 cc a moment calculation from the known refraction values would be absurd.\* Therefore we have assumed arbitrarily that the orientation polarization of isomer I is zero, i.e. that the distortion polarization is 113 cc. The moments in other solvents and at other temperatures have been calculated in this way to give " $\mu$  from  $R_D$ " in Table III. The moments calculated from the measured distortion polarization are shown as " $\mu$  from  $P_{e+a}$ ".

By either calculation it may be seen in Table III that the orientation polarization increases as the temperature is raised. Moreover, it is evident from the profound solvent effect that the moment values are only apparent ones. Nevertheless it seems reasonable to seek an explanation for an average moment of about 0.4 D at room temperature.

An adequate and authenticated explanation has not been found. But since we suspect from Dunitz' X-ray analysis that isomer I is inadequately described by a simple rigid centrosymmetrical structure we have chosen a model in which the cyclobutane ring is symmetrical and planar while the phenyl groups are randomly rotating, their planes at an angle ( $\alpha$ ) from linearity with the C-phenyl bond. This dynamic model will account for a dipole moment in isomer I.

The magnitude of this moment will depend on the group moment to be assigned to phenyl-C-hydrogen. The group moment for phenylalkyl seems to be 0.3–0.7 D depending upon the alkyl group (15). In consideration of cyclic substances a moment of 0.49 D has been reported for phenylcyclopropane in benzene at  $25^\circ$  (35) while the phenyl-carbon moment of the four methyl-substituted styrenes (36) would appear to be about 0.5 D.

The resultant moment may be calculated according to the relationship

$$\mu = 2(m) \sin \alpha$$

where  $m$  is the C-phenyl moment,  $\alpha$  is the angular deviation from linearity of the C-phenyl bond and the phenyl plane, and where all phenyl groups are rotating randomly.

\*It is of interest that tetraphenylethylene, which resembles tetraphenylcyclobutane in structural character, also would give an absurd value (Table III,  $-0.69$  D) for moment of  $20^\circ$  in benzene if the calculated value of molecular refraction were used. On the other hand the use of the measured distortion polarization (Table II) leads to a real and reasonable value of apparent moment in benzene which is augmented by measurement at  $40^\circ$ .

If  $m$  is taken as 0.5 then moments of 0.15 D, 0.30 D, and 0.50 D would require  $\alpha$  values of 10, 20, and 30° respectively. It is doubtful that the phenyl groups are inclined at even the smallest of these angles. Either the solvent effect is much greater than would be expected by the usual comparisons of the moments of vapors with those of solutions or else the model which we have assumed for tetraphenylbutane is incorrect. We suggest, as have others mentioned above, that the cyclobutane ring is not rigidly planar.

We have not been able to make a satisfactory calculation for the expected moment if the cyclobutane ring of isomer I is normally bent at a dihedral angle of 160°. However, our attempts do show us that a lesser deviation from C-phenyl linearity would be required than if the cyclobutane ring were planar in order to account for moment magnitudes of 0.1–0.4 D. It would seem that at the present time the experimental results can best be explained by non-planarity of the cyclobutane ring.

It may be seen in Table III that the apparent moments for isomer II are higher than those of isomer I. We have been unsuccessful in attempts to correlate mathematically the two sets of moments. This failure is not unexpected because entirely different sets of activated state conformations would maintain for the two isomers. However, the higher moment values of the ostensibly less symmetrical isomer II, over those of isomer I, show that both isomers are to some extent polar.

The authors wish to thank Mr. G. K. White for aid in the calculations and Dr. Dunitz for submission of samples used for X-ray diffraction studies. The chlorinated benzenes were kindly supplied by Dr. A. L. Rocklin of the Dow Chemical Company and by The Diamond Alkali Company. Funds for technical aid and for equipment have been furnished by the National Research Council to whom we are grateful. The generous co-operation of Dr. M. S. Newman and Dr. L. A. Wall are greatly appreciated.

## EXPERIMENTAL

### *Materials*

All of the substances listed in Tables I and III have been purified to constant melting point and in the case of liquids to constant refractive index. The hexachlorobenzene received from Dr. Rocklin was better than 99.5% pure; its Nujol mull absorbed at 3000 (S), 2850 (M shoulder), 1460 (W), 1378 (VW), 1340 (VS), 1297 (S), 930 (VW), 718 (VW), and 694 (S). The substituted styrenes have been purified according to a previous description (37). The tetraphenyl cyclobutanes were pure as received from Dr. Flood but were crystallized from methanol. The 1- $\downarrow$ -2 $\downarrow$ -3- $\uparrow$ -4 $\uparrow$ -isomer showed a diffraction pattern ( $\text{CuK}_\alpha$  radiation, Ni filtered) in Angstroms at relative intensities  $[I/I_1]$  as follows: [10]-5.34, 4.07[7]3.32[4]5.01[3]3.77[2]9.93, 8.50, 4.79[1]4.25, 3.90, 3.44, 3.16. The 1- $\downarrow$ -2,3,4- $\uparrow$ -isomer gave a pattern of [10]4.73[9]3.88[8]5.06, 3.78[6]5.77[4]9.06[3]3.19[2]10.84, 5.02[1]-3.56, 2.61 in contrast to the isomer of the same melting point (149°) isolated by Fulton (30) and sent to us by Dr. Dunitz. This sample showed [10]4.28[8]5.52[7]4.74[6]4.50[5]-5.86[4]6.96[2]10.35, 9.45, 2.76[1]4.92, 4.15, 4.00, 3.93, 3.56, 3.31.

### *Dielectric Constant Determinations*

The dielectric constants of solids were determined according to methods described previously (2, 3). It has been found that when a binder is necessary for preparation of satisfactory pellets polyethylene wax (10–30 microns diameter) is at least as satisfactory as korseal. However, a change of crystal habit, effected by recrystallization, usually renders the use of a binder unnecessary. Oftentimes good pellets are obtained by grinding unsatisfactory ones prior to repelletting. By this technique one is assured of random

orientation of the substance.

The dielectric constants of solutions were determined in the apparatus described previously (38) and also in a modification designed for determination of dielectric constant at a series of temperatures for each solution in order to reduce the time required for determination of temperature coefficients. The test cell was constructed from Corning No. 7740 glass. At the top of the inner concentric electrode was sealed through a Kovar metal rod to which connection could be made internally. On the outside of this electrode was burned in a gold paint (E.I. Du Pont No. 5732) compatible with the pyrex at 550° C. This metal coating which also covered the protruding Kovar rod as a resistance-free conductor was burnished and then polished with rouge (in turpentine) and then talc. The outside concentric electrode (0.7 mm clearance to give 60-pf capacitance when it was 23 mm I.D. by 85 mm long) was equipped at the top with an 8-mm diameter Kovar tube and was coated inside with gold as was described above so that a resistance-free connection could be made to ground from the outside of this metal tube. To the top of this Kovar tube was scaled a "burette" comprised of six 100-mm lengths of capillary tubing (0.8 mm I.D. graduated in millimeters) which were connected together by bulbs of 0.25-ml capacity. The two electrodes were ring-sealed together with an inlet tube at the bottom which terminated into a Kovar tube 0.9 mm O.D. of length sufficient to reach to the bottom of the pear-shaped flask (16-19 mm capacity) used previously for preparation and reference specific volume (at 25° C) of the test solution. A dry ice bath applied to the tapered bottom of this flask served to freeze and thus retain the solution within the test capacitor after it had been forced in by air pressure. If this apparatus were to be constructed again we would use Corning 7052 glass for the electrodes.

The solvent must be frozen and outgassed before use in this apparatus and the solution must finally be heated *in situ* at 5° above the highest temperature of the determination until no more bubbles appear; since at this time the level is slightly below the bottom of the burette the addition of a little more of the non-heated solution is necessary after cooling, but this amount does not supersaturate the test-cell content at the highest temperature of the determination. The temperature is maintained  $\pm 0.02^\circ$  by a surrounding jacket (also around the burette) containing refluxing carbon tetrachloride under a standard system for regulating pressure from 760 mm to 10 mm. The reflux system must be surmounted by a dry ice cooled condenser following a water condenser which follows an air condenser. The latter ensures that the refluxing carbon tetrachloride which pours down the jacket surrounding the burette is not too cold. The burette is best read by means of a cathetometer. It is recommended that the apparatus be calibrated by means of a non-aqueous solvent (benzene) since water tends to weaken the gold-glass bond.

Connection between the inner electrode and the resonance circuit of the variable frequency oscillator is made by a vertical threaded rod which meets the Kovar rod inside the electrode end-to-end inside of a close-fitting glass sleeve. The screw feed which advances the threaded rod to make contact is calibrated so as to reproduce inductance and capacitance in this switch and thus to maintain the precision of measurement to  $\pm 0.001$  pf.

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# ISOLATION AND CHARACTERIZATION OF A CELLULOSE FROM THE INNER BARK OF WHITE BIRCH (*BETULA PAPYRIFERA*)<sup>1</sup>

A. JABBAR MIAN AND T. E. TIMELL

## ABSTRACT

A pectic acid, a 4-*O*-methylglucuronoxylan, and a cellulose have been isolated from the inner bark of white birch (*Betula papyrifera*), in addition to minor amounts of other polysaccharides. The cellulose, which comprised 28% of the bark, yielded only D-glucose on hydrolysis, had a number-average degree of polymerization of 315 and, on methylation and hydrolysis, gave 2,3,6-tri-*O*-methyl-D-glucose and 2,3,4,6-tetra-*O*-methyl-D-glucose in a mole ratio of 59:1. The *O*-methylcellulose had a degree of polymerization of 125, thus suggesting the possibility of branching. Direct nitration of the bark gave a nitrate in a yield corresponding to 28% cellulose in the bark. Light-scattering measurements on this derivative indicated a weight-average degree of polymerization of 7500. While the low intrinsic viscosity of this nitrate did not exclude the possibility of branching, further evidence is needed to establish the linear or non-linear nature of birch bark cellulose.

Although it has been assumed for some time that cellulose is probably present in the inner bark of trees (1, 2), it was only recently that a pure, albeit degraded, cellulose was isolated from spruce bark (3). Since cellulose constitutes the most valuable part of a tree, it was considered to be of a certain interest to establish to what extent it is present in a hardwood bark and whether it is similar to the cellulose present in the wood. In a series of previous investigations (4-6), the isolation and properties of a cellulose from the wood of white birch (*Betula papyrifera* Marsh.) were studied. The present paper is concerned with the constitution and molecular properties of a cellulose from the inner bark (secondary phloem) of the same species.

## RESULTS AND DISCUSSION

The inner bark, which had been completely freed from cortex, cambium, and secondary xylem, was exhaustively extracted with organic solvents after which it was treated with hot water and subsequently with aqueous ammonium oxalate for removal of pectic material. Treatment with acid chlorite removed 25% of the extractive-free product. Subsequent extraction with aqueous potassium hydroxide resulted in isolation of a pure xylan (7). Alkaline borate removed a polysaccharide mixture and left a residue which could not be further fractionated and which corresponded to 28% of the bark. The yield and relative composition of the various fractions are given in Table I.

TABLE I  
Yield\* and carbohydrate composition† of bark fractions

Component	Yield	Galacturonic acid	Galactose	Glucose	Mannose	Arabinose	Xylose
Water extract	1.5	5	8	25	16	11	35
Pectic material	4.2	90	Trace	Nil	Nil	10	Nil
Glucuronoxylan	26.6	Trace	Nil	Trace	Nil	Nil	87‡
Alkali-borate extract	3.8	26	13	16	Nil	45	Nil
Cellulose	28.4	Nil	Nil	100	Nil	Nil	Trace

\*Percentage of original, extractive-free bark.

†Percentage of total reducing sugar content of each fraction.

‡In addition to 13% of 4-*O*-methylglucuronic acid.

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The predominant hemicellulose was a linear, (1  $\rightarrow$  4)- $\beta$ -linked 4-*O*-methylglucuronoxylan, containing on the average one (1  $\rightarrow$  2)- $\alpha$ -linked acid side chain per 10 xylose residues. Its number- and weight-average degrees of polymerization were 230 and 470, respectively (7). Water extracted a mixture of polysaccharides. The subsequent fraction consisted of a (1  $\rightarrow$  4)- $\alpha$ -linked pectic acid which could not be obtained free from arabinose residues. Alkaline borate removed a polysaccharide mixture, almost half of which consisted of arabinose residues.

The absolute composition of the bark in terms of sugar residues was computed from the total content of reducing sugar (54%) and the various amounts of polysaccharide residues present. The result is given in Table II. The carbohydrate content is consider-

TABLE II  
Carbohydrate composition of the extractive-free bark\*

Component	Galacturonic acid	Galactose	Glucose	Mannose	Arabinose	Xylose
Found†	2.2	1.1	28	Trace	2.7	21
Calculated‡	5.6	0.6	29	0.2	2.3	23

\*Percentage of oven-dry material.

†Found by direct analysis of the bark.

‡Calculated from yield and composition of the fractions.

ably higher than that previously reported (8) for the entire bark of the same species, but the relative composition is approximately the same. The directly determined values were also compared with those which could be calculated from the percentage and composition of the various fractions. Except for the galacturonic acid and galactose residues, the agreement is good, thus indicating that the entire polysaccharide portion of the bark had been accounted for in the fractions isolated.

The residual material, a white powder, was insoluble in aqueous alkali, yielded only D-glucose on hydrolysis, and consumed 1 mole of periodate per glucose residue. Its X-ray powder diagram and infrared spectrum were identical to those of cellulose II. The polysaccharide was methylated to completion and hydrolyzed. The resulting sugar mixture was resolved on a charcoal-Celite column by gradient elution with aqueous ethanol to yield 2,3,6-tri-*O*-methyl-D-glucose (59 parts) and 2,3,4,6-tetra-*O*-methyl-D-glucose (1 part), both of which were obtained crystalline. The number-average degree of polymerization ( $\bar{P}_n$ ) of the *O*-methylcellulose, as determined by osmometry, was 125, thus suggesting the presence of 2.1 non-reducing end groups per average molecule.

The cellulose was converted to its nitrate derivative with an acid mixture known to cause little or no depolymerization of polysaccharides (9; 10). Osmotic pressure measurements on the nitrate indicated a  $\bar{P}_n$  value of 315. It is well known that cellulose suffers degradation under the action of both acid chlorite (4) and alkali (11). It was evident therefore that the  $\bar{P}_n$  value obtained could hardly represent the molecular weight of the cellulose as it originally occurred in the bark. Direct nitration of wood with the above acid mixture has been shown (12) to result in the isolation of cellulose nitrates in almost quantitative yield, while nitrated pectic acid and hemicelluloses are largely removed. When the extractive-free bark was subjected to a similar treatment, both before and after removal of pectic material, cellulose nitrates were obtained in yields corresponding to 25–28% cellulose in the bark. Denitration, followed by hydrolysis, indicated the presence of glucose and traces of xylose residues. The intrinsic viscosities



of the nitrates showed that they possessed molecular weights much higher than that of the material remaining after complete extraction of the bark.

The nitrate from the pectin-free bark was subjected to light-scattering measurements in acetone solution, essentially as reported previously (13). The results were evaluated according to Zimm (14) and gave a weight-average molecular weight of  $2.17 \times 10^6$ , corresponding to a degree of polymerization ( $\bar{P}_w$ ) of 7500, and a root-mean-square Z-average radius of gyration of 1730 Å. The corresponding values for the cellulose present in the wood of the same species were  $2.73 \times 10^6$ , 9400, and 1770 Å, respectively (13).

It is evident from the isolation of D-glucose and 2,3,6-tri-O-methyl-D-glucose that the polysaccharide was a (1 → 4)-linked glucoglycan, and that the 2,3,4,6-tetra-O-methyl-D-glucose originated from the non-reducing end groups. Since the polysaccharide did not give any color with iodine, starch was absent. The infrared spectrum suggested the presence of β-pyranosidic bonds (15). The polysaccharide was therefore probably cellulose. This conclusion was corroborated by the fact that its X-ray diffraction pattern coincided with that of cellulose II. Birch bark cellulose apparently has a molecular weight somewhat lower than that of the cellulose in the wood of the same species. The range involved, 7500–9500, is that typical of most native celluloses from various natural sources (16, 17). The yields on nitration agreed excellently with the amount obtained after complete removal of non-cellulosic polysaccharides and also compared well with the known glucose content of the bark. It is probable therefore that the bark contained approximately 28% cellulose. Bark from white spruce has previously (3) been reported to contain at least 16% cellulose.

In a previous study (17), a relationship was developed between the intrinsic viscosity and weight-average degree of polymerization of cellulose nitrates as determined by light scattering. According to this equation, the intrinsic viscosity of the present nitrate (33.0 dl/g at trisubstitution) should correspond to a degree of polymerization of only 4300, much lower than the directly determined value of 7500. This fact suggests the presence of a branched polysaccharide, since a branched macromolecule exhibits an intrinsic viscosity lower than that of a linear polymer of the same molecular weight (18–20). That branching might be involved is also suggested by the fact that the degraded O-methylcellulose contained 2.1 non-reducing end groups, corresponding to 1.1 branch points per average molecule.

If branching had occurred, however, the ratio of the root-mean-square radius of gyration to the Z-average molecular weight would have been expected to be lower than the value computed (0.90) (18, 21). The evidence is accordingly equivocal and more information is necessary before any statement can be made as to the linear or branched nature of birch bark cellulose. All other native celluloses so far studied have been found to be linear.

#### EXPERIMENTAL

All specific rotations are equilibrium values and were determined at 20° C unless otherwise stated. Melting points are corrected. Evaporations were carried out *in vacuo* at 40–50° C.

##### *Paper Chromatography*

Solvents (v/v) used for separating sugars were (A) ethyl acetate:acetic acid:water (9:2:2), (B) butan-1-ol:pyridine:water (10:3:3), and (C) butanone:water (89:11). Separations were carried out by the descending technique on Whatman No. 1 filter paper and with o-aminodiphenyl as the spray reagent (22).

### *Analytical Methods*

The bark was analyzed by standard methods developed for wood (23). A portion of the bark was hydrolyzed to completion (24) and the reducing sugar content of the hydrolyzate was determined by the *o*-aminodiphenyl method (22). Corrections were applied for the different rates of hydrolysis of the sugars (24) and the polysaccharide content was calculated from the relative amounts of the various sugar residues present. The ratios between the sugars present were estimated after quantitative separation by paper chromatography (solvents A and B) (22).

### *Isolation of the Bark*

An autumn-felled specimen of a healthy white birch was immediately immersed in aqueous ethanol for several days after which the outer bark was easily removed. The brown, inner bark was separated manually from the cambium and the wood, was treated with boiling methanol, and was dried in the air. The tree contained 3.8% outer and 10.4% inner bark, based on the oven-dry weight of the trunk. The bark was converted to sawdust and the 20- to 80-mesh fraction was collected. Anal. Klason "lignin", 28.6; pentosan, 26.7; ash, 5.2; uronic anhydride, 6.9; and polysaccharides, 54%. Successive extractions with ethanol-benzene (1:2 v/v), methanol, and acetone removed 3.2, 0.8, and 0.7%, respectively. Water extracted 6.0% of material.

### *Isolation of Polysaccharides*

A detailed description of this isolation has been given elsewhere (7). Treatment of the bark with hot water removed a mixture of polysaccharides corresponding to 1.5% of the extractive-free bark. Further extraction with hot, aqueous 0.5% ammonium oxalate gave 4.5% of a pectic material composed of galacturonic acid together with minor quantities of arabinose. At this point, the residual bark was digested with acid chlorite which removed 25.0% of material, mostly of non-carbohydrate nature. Subsequent extraction with 24% aqueous potassium hydroxide resulted in the isolation of a pure 4-*O*-methylglucuronoxylan (7) in a yield of 26.6%. When the remaining material was extracted with 17.5% sodium hydroxide containing 4.0% boric acid (25, 26), a mixture of polysaccharides was obtained (3.8%). After exhaustive washing with alkali and water, the remaining portion was acidified with dilute acetic acid and was washed until neutral with water and then with ethanol and petroleum ether (b.p. 30–60° C). Drying *in vacuo* over potassium hydroxide yielded a white powder, corresponding to 28.4% of the extractive-free bark. The yield and composition of each fraction are given in Table I.

### *Characterization of the Cellulose*

The infrared spectrum of the cellulose showed a maximum at 886  $\text{cm}^{-1}$ , indicative of the presence of  $\beta$ -pyranosidic bonds (15).

A portion of the cellulose (1.0 g) was hydrolyzed to yield a sirup (0.9 g). Paper chromatography (solvents A and B) indicated the presence of glucose and a faint trace of xylose. On standing, the sirup crystallized,  $[\alpha]_D +53^\circ$  (*c*, 5.3 in water), m.p. and mixed m.p. 144–145° C. The *p*-nitroaniline derivative had a melting point of 182° C (27).

The X-ray powder diagram was determined with a Seifert X-ray unit. The radiation used was nickel-filtered  $\text{Cu } K_\alpha$ . The following interplanar lattice spacings ( $\text{\AA}$ ) were obtained: 4.2 (s), 3.0 (w), 2.5 (w), and 2.3 (w). An authentic sample of cellulose II had the following distances: 4.1 (s), 3.1 (w), 2.6 (w), and 2.2 (w). Both diagrams were in accord with published data (28).

### Periodate Oxidation of the Cellulose

Dry cellulose (150 mg) was dispersed in 0.05 *M* sodium metaperiodate (50.0 ml) and shaken in the dark at +30° C for various lengths of time. The consumption of periodate was determined by the excess arsenite method. The following moles of oxidant were consumed per glucose residue (days): 0.79–2, 0.89–3, 1.02–5, 1.04–7, 1.05–8, 1.06–9, 1.07–10. Extrapolation of the later part of the conversion–time curve to zero time gave the consumption of periodate,  $1.00 \pm 0.02$  moles per glucose residue.

### Methylation of the Cellulose

Cellulose (20 g) was dispersed in 40% (w/w) aqueous sodium hydroxide (400 ml) in an atmosphere of nitrogen, and dimethyl sulphate (250 ml) was added dropwise over a period of 20 hours. This process was repeated three times. Solid sodium hydroxide (200 g) was added, followed by dimethyl sulphate (dropwise, 250 ml). This treatment was repeated nine times, water being added whenever necessary for efficient stirring. The mixture was neutralized with concentrated sulphuric acid to pH 4, diluted, and heated to 90° C. The precipitated, partly methylated cellulose was recovered by filtration, washed with hot water, and dried *in vacuo* to give a hard powder (17.5 g).

The product was dissolved in dry dimethyl formamide (250 ml) and treated with methyl iodide (50 ml) and silver oxide (50 g) at room temperature for 24 hours (29). This process was repeated three times. The solid residue was exhaustively extracted with chloroform and the resulting suspension was centrifuged. The chloroform solution was then washed with 5% aqueous potassium cyanide (29) and water. After drying over anhydrous sodium sulphate, the solution was concentrated to 200 ml and added slowly to petroleum ether (1.5 liters). The precipitate formed was recovered by filtration, washed with petroleum ether, and dried to yield a white powder (10.2 g). Anal. Calc. for a fully methylated cellulose:  $[C_6H_7O_2(OCH_3)_3]_n$ : OCH<sub>3</sub>, 45.6%. Found: OCH<sub>3</sub>, 44.5%.

Three further methylations according to Purdie (30) failed to increase the methoxyl content of the product (31). Its infrared diagram suggested the presence of hardly any hydroxyl groups.

### Methanolysis and Hydrolysis of the Methylated Cellulose

A portion of the methylated cellulose (3.0 g) was boiled under reflux with 0.7 *N* methanolic hydrogen chloride (75 ml) for 7 hours. The methanol was partly evaporated and the residue was boiled under reflux with *N* hydrochloric acid (75 ml) for 7 hours. After neutralization with silver carbonate, filtration through Celite, treatment with hydrogen sulphide, and filtration, evaporation gave a sirup (2.8 g). Paper chromatography (solvent C) suggested the presence of a trace of a di-*O*-methylhexose, a tri-*O*-methylhexose, and a small amount of a tetra-*O*-methylhexose.

### Separation of the Methylated Glucoses

A portion of the methylated sugar mixture (0.90 g) was added to the top of a Darco G-60 charcoal–Celite (1:1 w/w) column (3.5 × 55 cm) (32) and resolved by gradient elution (33, 34) with 3 liters each of 5% aqueous ethanol → 25% ethanol and 25% ethanol → 40% ethanol. Fractions, 25 ml each, were collected at a rate of 50 ml/hr. Every third fraction was examined by paper chromatography (solvent C). Only two main fractions were obtained, a tri-*O*-methylglucose (790 mg) and a tetra-*O*-methylglucose (14.7 mg).

### Identification of 2,3,6-Tri-*O*-methyl-D-glucose

This fraction, the first to be eluted from the column, crystallized spontaneously. After

recrystallization from ethyl ether, the melting point was 119–120° C, undepressed on admixture with an authentic sample of 2,3,6-tri-*O*-methyl-D-glucose,  $[\alpha]_D +68^\circ$  (*c*, 2.0 in water) (35).

*Identification of 2,3,4,6-Tetra-O-methyl-D-glucose*

On recrystallization from petroleum ether, this fraction had a melting point of 54–55° C (36),  $[\alpha]_D +25^\circ \rightarrow +82^\circ$  (equilibrium, *c*, 1.0 in water).

*Nitration of the Cellulose*

Dry cellulose (31.0 g) was added in small portions and with vigorous stirring to a mixture of nitric acid, phosphoric acid, and phosphorous pentoxide (64:26:10, w/w) (11) cooled to –5° C. The reaction was allowed to proceed in the dark at +17° C for 1.5 hours (12). After removal of most of the acid mixture by filtration through fritted glass, the nitrated product was washed with ice water until neutral and then with methanol. Drying *in vacuo* gave a white powder (46.5 g, 88%) with a nitrogen content (37) of 13.10%, corresponding to a degree of substitution of 2.61.

*Determination of the Number-Average Molecular Weight of the Methylated and Nitrated Celluloses*

Osmotic pressure measurements were carried out at +30° C as described previously (38) with modified (39) Zimm-Myerson (40) osmometers and gel cellophane membranes. The solvent for the methylated cellulose was a 9:1 mixture (v/v) of chloroform and ethanol and for the nitrate, *n*-butyl acetate. The results are summarized in Table III.

TABLE III  
Osmometry data

O-Methylcellulose			Cellulose nitrate		
<i>w</i> *	<i>h</i> †	<i>h/w</i>	<i>w</i>	<i>h</i>	<i>h/w</i>
2.416	2.680	1.109	5.373	1.645	0.306
1.967	1.998	1.016	4.301	1.120	0.260
1.817	1.921	1.057	3.220	0.990	0.307
1.312	1.362	1.038	2.155	0.629	0.292
1.134	1.202	1.060	1.146	0.362	0.316
0.646	0.656	1.015	1.063	0.315	0.296
0	—	1.01	0	—	0.29

\*Concentration in grams/kilograms solution.

†Osmotic height in centimeter solution.

*Isolation of Cellulose by Direct Nitration of the Bark*

Dry birch bark (20.0 g), previously extracted with hot water and aqueous ammonium oxalate, was treated with the nitrating mixture referred to above (400 g) at +17° for 5 hours. Most of the acid mixture was removed by filtration and the solid residue was washed immediately with a 1:1 mixture of acetic acid and water cooled to –16° C (4 liters). The product was washed successively with water, with saturated sodium bicarbonate, with 10% aqueous acetic acid, and finally with water until the filtrate was neutral. A part of the nitrated, non-carbohydrate material was removed by extraction with methanol. The residue was dissolved in acetone (2 liters) and solid material was removed on the centrifuge. The clear solution was poured into water and the precipitate was washed with water and methanol and dried *in vacuo* at room temperature to give a white, fibrous material (A, 9.3 g, 25.0%). Nitrogen content: 13.73%, corresponding to a degree of substitution of 2.84.

A similar treatment of the extractive-free bark before removal of pectic material (20.0 g) gave a similar cellulose nitrate (B, 8.8 g, 26.0%). Nitrogen content: 13.72%. Nitration of the same product for 24 hours gave a nitrate in a yield of 28.1%.

A portion of nitrate A was treated with 20% ammonium hydrosulphide at room temperature for 7 hours (41). The denitrated product was hydrolyzed and examined by paper chromatography (solvents A and B). Only glucose and traces of xylose residues were present.

#### *Determination of the Intrinsic Viscosity of the Cellulose Nitrates*

The instrument used was a Craig-Henderson viscometer (42). The temperature was  $+30^{\circ}\text{C}$  and the solvent was *n*-butyl acetate. Measurements were carried out as described previously (17). No corrections were applied for shear dependence. The logarithm of the relative viscosities, when plotted against concentrations, gave linear relationships which were extrapolated to zero concentration to yield the intrinsic viscosities. The values obtained were 28.5 and 24.6 dl/g (nitrates A and B), corresponding to 33.0 and 28.1 dl/g at trisubstitution (43).

#### *Determination of the Weight-Average Molecular Weight of Cellulose Nitrate A*

Light-scattering measurements were carried out essentially as described previously (13). The solvent was freshly redistilled acetone, b.p.  $56.3\text{--}56.8^{\circ}\text{C}$ . After ultracentrifugation at 140,000 g for 3 hours, the polymer solution (0.1%) was transferred to a light-scattering cell especially designed for eliminating both floating and sedimenting debris (44). The cell was subjected to ultracentrifugation at 35,000 g for 1 hour and then transferred directly to the photometer, a Brice-Phoenix instrument which had been considerably modified (46). Scattering intensities were measured at angles from  $35^{\circ}$  to  $135^{\circ}$  relative to the incident beam and at different concentrations. The refractive index increment had previously been estimated as 0.105 ml/g (21). Concentrations were determined by precipitating several aliquots of the original solution into water. The fibrous precipitate was washed with water and methanol and dried *in vacuo* at  $+60^{\circ}\text{C}$  for 3 hours.

Zimm plots (14) were obtained in the usual way by plotting  $Kc/R_{\theta}$  versus  $\sin^2 \theta/2 + 2000c$  where  $K = 2\pi^2 n_0^2 (dn/dc)^2 N \lambda^4$  and the symbols have their usual significance (21). The weight-average molecular weight,  $\bar{M}_w$ , was obtained from the relationship

$$\bar{M}_w = 1/(Kc/R_{\theta})_{c, \theta=0}.$$

The corresponding degree of polymerization,  $\bar{P}_w$ , was calculated from the relationship  $\bar{P}_w = \bar{M}_w/M_r$  where  $M_r$  was the molecular weight of the nitrated glucose residue (290). The root-mean-square *Z*-average radius of gyration,  $\sqrt{s_z^2}$ , was computed from the initial slope of the  $c = 0$  line in the Zimm plot according to the relationship (21)

$$\frac{\text{initial slope}}{\text{intercept}} = (16\pi^2/3) \cdot s_z^2 (n_0/\lambda)^2.$$

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# STERIODS AND RELATED PRODUCTS

## XIV. THE SYNTHESIS OF 17 $\alpha$ -HALOGENATED 20,21-KETOLS OF THE CORTICOID TYPE<sup>1,2</sup>

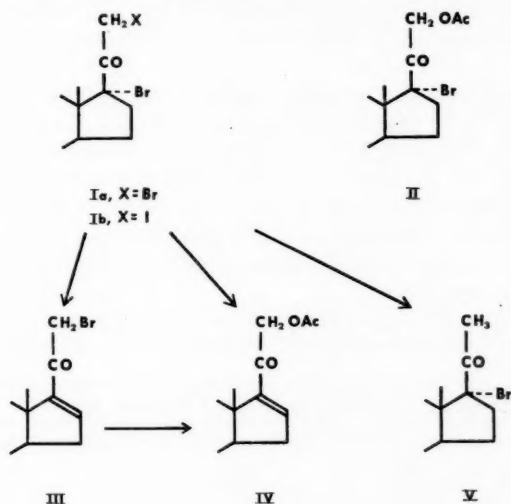
CH. R. ENGEL, R.-M. HOEGERLE,<sup>3</sup> AND R. DEGHENGI

### ABSTRACT

In continuation of previous work, the hindering effect of 17 $\alpha$ -substituents on replacement reactions in position 21 of the steroid molecule was further studied. It is shown that the impossibility of replacing a 21-halogen substituent by an acetoxy group in the presence of a bromine atom in position 17 $\alpha$  is due both to a steric effect of the bulky 17-substituent and to its facile elimination. It is further shown that the replacement reaction in 21 may be carried out in the presence of the smaller and less readily eliminated 17 $\alpha$ -chlorine substituent. In connection with these investigations, 17 $\alpha$ -chloro-11-dehydrocorticosterone, the 17-chloro analogue of cortisone, was synthesized. The introduction of a chlorine atom into position 17 lowers the glucocorticoid activity.

In a recent publication of this series (2) we reported the synthesis of 17 $\alpha$ -bromo-11-dehydrocorticosterone, the first 17-halogenated glucocorticoid. In that synthesis, the halogen substituent was introduced subsequent to the elaboration of the ketol side chain.

At first sight it would have appeared attractive to transform a readily available 17,21-dihalogenated 20-ketone (compare partial formula I) to a 17-bromo-21-acetoxy ketone (compare II) by the classical reaction with an alkali acetate. However, it was known from earlier work by Plattner, Heusser, and Angliker (3) that treatment of a 17,21-dibromo-20-ketone (Ia), with potassium acetate in acetic acid, led predominately



to elimination of hydrogen bromide in positions 16-17, without replacement of the 21-bromine atom (compare III). The elimination of hydrogen bromide from a tertiary

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Contribution from the Department of Chemistry, Laval University, Quebec, Que. Some of the results reported in this paper were included in a communication presented before the 4th International Congress of Biochemistry, Vienna, September, 1958; other results were in a paper presented before the 17th Congress of the French-Canadian Association for the Advancement of Science, Montreal, October, 1959.

<sup>2</sup>For paper XIII of this series see reference 1.

<sup>3</sup>N.R.C. Postdoctorate Fellow, 1958-59.

bromide, in conjugation with a carbonyl group, is of course easily understood. On the other hand, it seems plausible to assume that in the presence of as bulky a 17-substituent as a bromine atom, the replacement of the halogen group in 21, by acetate, should present considerable difficulties, since it is known that a 17-methyl group seriously hinders reactions in this position (4-8). Plattner and co-workers (3) showed that an unsaturated bromide of type III can be converted to the 21-acetate by treatment with potassium acetate in acetic acid, in the presence of acetic anhydride, and that a 17,21-dibromide (compare Ia) can be transformed, under analogous conditions, directly but in low yield to the same unsaturated ketol acetate (compare IV). It seems reasonable to assume that in this reaction the unsaturated bromide (compare III) is an intermediate and, hence, that the dehydrobromination precedes the substitution in 21.<sup>4</sup>

In the course of the present study, we investigated the reaction of an iodo bromide of type Ib [17 $\alpha$ -bromo-21-iodo-3 $\alpha$ -acetoxy-11,20-dioxopregnane (Ic, see Experimental)] with potassium acetate in boiling acetone. After 1 hour, the starting material was recovered practically unchanged, which seems in accord with the assumption that the bulky 17-bromine substituent hinders the replacement reaction in 21. After prolonged treatment, reduction of the 21-iodine substituent occurred, leading to the 17 $\alpha$ -bromo-21-methyl-20-ketone (compare V), as well as partial elimination of hydrogen bromide, evidenced by the  $\Delta^{16}$ -20-ketone chromophore detected in the mother liquors of the reaction product. Absolutely no replacement of the halogen in 21 by an acetoxy group had taken place.

In summary, the 21-halogen atom of a 21-halo-20-ketone cannot be replaced by an acetoxy group in the presence of a 17 $\alpha$ -bromine substituent (with preservation of the latter), because of both the steric effect of the bulky 17-bromine substituent and competing reactions.

We considered that the situation would be different in the case of a 17 $\alpha$ -chlorine substituent. Indeed, the smaller chlorine atom should exert a smaller steric effect and should not lend itself with the same ease to an elimination reaction as a bromine substituent.

In order to prove this assumption, we subjected 21-bromo-17 $\alpha$ -chloro-3 $\alpha$ -hydroxy-11,20-dioxopregnane (XI) to the action of potassium acetate in the presence of potassium iodide; as we had expected, the 21-acetoxy-17-chloro-20-ketone IX was formed without difficulty. We thus established further evidence of the fact that a bulky group in position 17 hinders reactions in position 21.<sup>5</sup>

The 21-bromo-17-chloro-20-ketone XI employed in this reaction was readily obtained from 3 $\alpha$ -acetoxy-11,20-dioxopregnane (VI).<sup>6</sup> Whereas the 17 $\alpha$ -chloride VIII can be

<sup>4</sup>When a 17-bromo-21-iodo ketone (compare Ib) is treated with silver acetate in pyridine, in the presence of acetic anhydride—conditions which allow the replacement of a 21-iodine substituent by an acetoxy group in the presence of a 17-methyl group (compare 7 and 8)—reduction in position 21 occurs, the reaction leading to a mixture composed of a  $\Delta^{16}$ -20-ketone (compare i) and an aromatic rearrangement product of type ii (6).



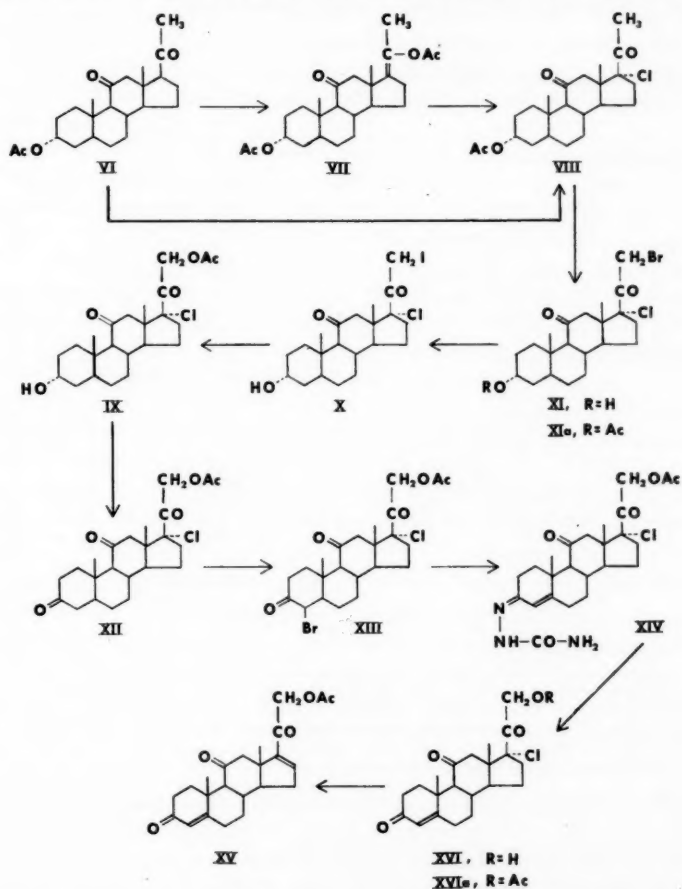
<sup>5</sup>It should be pointed out that even in the presence of a relatively small hydroxy substituent in position 17, the substitution in 21 proceeds less readily than in the case of a 17-unsubstituted product (compare for instance 9).

<sup>6</sup>We are indebted to the Schering Corporation, Bloomfield, New Jersey, for the generous gift of this starting material.

produced by direct chlorination of VI, a much better product was obtained by chlorination of the mono-enol acetate VII. We synthesized the latter product, previously described by Anderson *et al.* (10), either by reaction of VI with isopropenyl acetate and sulphuric acid followed by chromatography, or, even more conveniently, by Barton's method (11) with acetic anhydride and perchloric acid. Using the latter procedure both geometric isomers of VII were isolated.<sup>7</sup>

The 17-chloro-20-ketone VIII was readily brominated in 21 (XIa), with molecular bromine in acetic acid, at 60°. Hydrolysis of the acetate with perchloric acid in methanol (12 and 13) gave the 3-hydroxy chloro bromide XI, which, as stated above, can be transformed in good yield to the corresponding 21-acetate IX.

Since our group has been interested for some time in the influence of the chemical nature of the 17 $\alpha$ -substituent on hormonal activities (compare, for instance, 1, 2, 7, 13, 14, 15, 16, 17, 18), we considered it attractive to convert the 17 $\alpha$ -chloro-21-acetoxy-20-ketone IX to the 17-chloro analogue of cortisone (XVI). The synthesis followed classical



<sup>7</sup>In our hands the method of Anderson *et al.* (10) for the preparation of VII from VI, using acetic anhydride and an acid catalyst in toluene, gave unsatisfactory results.

<sup>8</sup>We established in preliminary experiments that bromination in chloroform was not satisfactory.

lines. Oxidization of IX with chromic acid and sulphuric acid (19, 20) gave the triketone XII which was transformed via the 4-bromide XIII and the semicarbazone XIV (compare 21) to the 4-unsaturated acetate XVIa, readily hydrolyzed with perchloric acid in methanol (12, 13) to 17 $\alpha$ -chloro-11-dehydrocorticosterone (XVI). The free alcohol XVI was easily reacylated to XVIa and the position of the chlorine substituent was proved by conversion of the latter, with dimethylformamide and potassium iodide, to 17-anhydrocortisone acetate (XV) (22).<sup>9</sup> The  $\alpha$ -configuration of the 17-substituent was assumed in analogy with the proved configuration of the corresponding bromides (compare 23).

It is of interest to note that 17 $\alpha$ -chlorination of a 20-ketone causes a marked levorotatory shift, which is, however, not quite as pronounced as the one brought about by 17-bromination (1, 2, 13, 24). In Table I we have computed representative molecular rotational differences produced by various substitutions of 20-ketones in position 17; values for hydroxy, methyl, chlorine, and bromine derivatives are given. It can be seen that all these substitutions lead to a levorotatory shift and that the strength of the effect increases in the order in which the substituents are mentioned above.

TABLE I  
Molecular rotational differences of 17 $\alpha$ -substituted 20-keto steroids<sup>a</sup>

Product	$[M]_D$	$[M]_D^{17\alpha\text{-der.}} - [M]_D^{17\alpha\text{-H}}$
3 $\alpha$ -Acetoxy-11,20-dioxopregnane	495 <sup>ob</sup> 455 <sup>o</sup> (acetone) <sup>c</sup>	
17 $\alpha$ -Hydroxy-	330 <sup>o</sup> (acetone) <sup>d</sup>	-125 <sup>o</sup> (acetone)
17 $\alpha$ -Chloro-	85 <sup>oe</sup>	-410 <sup>o</sup>
17 $\alpha$ -Bromo-	5 <sup>of</sup>	-490 <sup>o</sup>
3 $\alpha$ -Hydroxy-21-acetoxy-11,20-dioxopregnane	425 <sup>o</sup> (acetone) <sup>g</sup> 320 <sup>o</sup> (acetone) <sup>h</sup>	-105 <sup>o</sup>
17 $\alpha$ -Hydroxy-	50 <sup>oe</sup>	-375 <sup>op</sup>
17 $\alpha$ -Chloro-	20 <sup>of</sup>	-405 <sup>op</sup>
21-Acetoxy-3,11,20-trioxopregnane	425 <sup>oa</sup> 405 <sup>o</sup> (acetone) <sup>i</sup> 335 <sup>o</sup> (acetone) <sup>j</sup>	-70 <sup>o</sup> (acetone)
17 $\alpha$ -Hydroxy-	185 <sup>oa</sup>	-240 <sup>o</sup>
17 $\alpha$ -Methyl-	65 <sup>oe</sup>	-360 <sup>o</sup>
17 $\alpha$ -Chloro-	0 <sup>of</sup>	-425 <sup>o</sup>
17 $\alpha$ -Bromo-		
$\Delta^4$ -21-Acetoxy-3,11,20-trioxopregnene	925 <sup>oi</sup> 860 <sup>om</sup>	-65 <sup>o</sup>
17 $\alpha$ -Hydroxy-	680 <sup>ok</sup>	-245 <sup>o</sup>
17 $\alpha$ -Methyl-	440 <sup>os</sup>	-485 <sup>o</sup>
17 $\alpha$ -Chloro-	435 <sup>of</sup>	-490 <sup>o</sup>
17 $\alpha$ -Bromo-		
$\Delta^4$ -21-Hydroxy-3,11,20-trioxopregnene	890 <sup>o</sup> (EtOH) <sup>n</sup> 760 <sup>o</sup> (EtOH) <sup>o</sup>	-130 <sup>o</sup>
17 $\alpha$ -Hydroxy-	625 <sup>ok</sup>	-265 <sup>op</sup>
17 $\alpha$ -Methyl-	535 <sup>oe</sup>	-355 <sup>op</sup>
17 $\alpha$ -Chloro-	360 <sup>of</sup>	-530 <sup>op</sup>
17 $\alpha$ -Bromo-		

<sup>a</sup>The molecular rotations were calculated to the nearest 5°. When not otherwise specified, rotations were taken in CHCl<sub>3</sub>.

<sup>b</sup>Means of values reported in references 25 and 26. <sup>c</sup>Reference 27. <sup>d</sup>Reference 28. <sup>e</sup>Experimental. <sup>f</sup>Reference 2. <sup>g</sup>Reference 29. <sup>h</sup>Reference 30. <sup>i</sup>Reference 31. <sup>j</sup>Means of values given in references 28 and 32. <sup>k</sup>Reference 15. <sup>l</sup>Reference 33. <sup>m</sup>Reference 34. <sup>n</sup>Reference 35. <sup>o</sup>Means of values given in references 34 and 36. <sup>p</sup>The values can only be considered as indicative because comparisons were made between rotations in different solvents.

Dr. P. Perlman and Dr. S. Tolksdorf of Bloomfield, New Jersey, kindly tested the new hormone analogue XVI and its acetate XVIa in their eosinophil assay and found that the products had the same order of activity as their bromo analogues (2). A detailed account of the biological investigations is to be published elsewhere. The preliminary

<sup>9</sup>We wish to thank sincerely Dr. S. Bernstein for kindly providing us with an authentic sample for comparison.

results confirm that the electronegativity of the  $17\alpha$ -substituent is not, at least to an appreciable extent, an enhancing factor of glucocorticoid and related corticoid activities (compare 2).<sup>10</sup>

#### EXPERIMENTAL<sup>11, 12, 13</sup>

##### *Reaction of 17 $\alpha$ -Bromo-21-iodo-3 $\alpha$ -acetoxy-11,20-dioxopregnane (Ic) with Potassium Acetate in Acetone*

(a) A quantity of 1.5 g of 17 $\alpha$ ,21-dibromo-3 $\alpha$ -acetoxy-11,20-dioxopregnane was transformed in the usual fashion to 17 $\alpha$ -bromo-21-iodo-3 $\alpha$ -acetoxy-11,20-dioxopregnane (Ic) (compare the procedure described in reference 3), by treatment with 0.5 g of sodium iodide in 150 cc of boiling acetone. To the cooled solution was added potassium acetate, freshly prepared from 6 g of potassium bicarbonate and 3.5 cc of acetic acid, and the mixture was refluxed under nitrogen for 1 hour. The volume of the solution was reduced *in vacuo* and the organic product was precipitated in water. The mixture was extracted with dichloromethane, the organic solution was washed with water and was dried over sodium sulphate. Removal of the solvent gave 1.6 g of almost colorless crystals, m.p. 163–170° decomp.; the melting point was not depressed upon admixture of iodide Ic. The product gave a positive iodine test and the infrared spectrum corroborated the identity of the product with iodide Ic.

(b) A quantity of 1.485 g of 17 $\alpha$ ,21-dibromo-3 $\alpha$ -acetoxy-11,20-dioxopregnane was transformed with 1.5 g of sodium iodide in 250 cc of acetone to the bromo iodide Ic. To this solution, potassium acetate, freshly prepared from 12 g of potassium bicarbonate and 7 cc of acetic acid, was added and the mixture was refluxed for 24 hours. The colorless solution (which had been yellow at the beginning of the reaction) was cooled and poured into cold water. The precipitate was extracted with dichloromethane, the organic layer was washed with water and dried over sodium sulphate. Removal of the solvent gave 1.4 g of an oil which, upon crystallization from dichloromethane–ether–hexane, gave 350 mg of colorless crystals, m.p. 150–155° decomp. Recrystallization from ether raised the melting point to 156–158° decomp. The infrared spectrum of the product was identical with that of authentic 17 $\alpha$ -bromo-3 $\alpha$ -acetoxy-11,20-dioxopregnane (15) and the mixed melting point showed no depression upon admixture of authentic material.

The mother liquors of the crystallized product showed in the infrared the typical absorption of a  $\Delta^{16}$ -20-ketone ( $\nu_{\text{max}}^{\text{CHCl}_3}$  1592 and 1665  $\text{cm}^{-1}$ ) and no absorption band attributable to a 21-acetoxy group.

##### $\Delta^{17(20)}$ -3 $\alpha$ ,20-Diacetoxy-11-oxopregnene (VII)

(a) A solution of 1.5 g of 3 $\alpha$ -acetoxy-11,20-dioxopregnane (VI) in 5 cc of isopropenyl acetate was refluxed for 2 hours with 0.1 cc of concentrated sulphuric acid. The mixture was cooled and extracted with ether; the ethereal solution was washed with sodium bicarbonate solution and with water and was dried over sodium sulphate. The solvent was removed and the product (1.6 g) was chromatographed on 50 g of aluminum oxide

<sup>10</sup>Drs. H. L. Herzog, M. Jevnik Gentles, H. M. Marshall, and E. B. Hershberg informed us of their independent synthesis of 17 $\alpha$ -chloro-11-dehydrocorticosterone acetate (XVIa) by a different route. It was agreed that their article should appear in the *Journal of the American Chemical Society* simultaneously with the present one in this journal.

<sup>11</sup>The melting points were taken in the evacuated capillaries and the temperatures were corrected.

<sup>12</sup>The microanalyses were performed by Dr. O. Schwarzkopf, New York, N. Y., and by Dr. Alfred Bernhardt, Mülheim (Ruhr). We wish to express to them and their associates our sincere appreciation.

<sup>13</sup>For chromatography we used Davison's silica gel No. 923, Woelm's aluminum oxide, activity II–III, and Merck's aluminum oxide treated as described under footnote 31 of reference 7. We wish to thank Merck and Co., Montreal, for a generous gift of this material.

(pH 6.5). Petroleum ether - benzene mixtures eluted 500 mg of the enol diacetate VII, m.p. 99-110°. Benzene eluted 600 mg of starting material (VI), m.p. 124-126°, not depressed upon admixture of authentic VI; the product was further identified by comparison of the infrared spectra. Considering the recovery of the starting material, the yield of VII from VI was 55%.

A portion of the enol diacetate VII was recrystallized four times from acetone-hexane for analysis: silky needles, m.p. 127.5-129.5°,  $[\alpha]_D^{26} +56^\circ$  ( $c$ , 1.0 in  $\text{CHCl}_3$ ),  $\nu_{\text{max}}^{\text{KBr}}$  1220, 1245  $\text{cm}^{-1}$  (acetates), 1695  $\text{cm}^{-1}$  (11-ketone), 1722 and 1730  $\text{cm}^{-1}$  (shoulder) (acetates); positive tetranitromethane reaction. Anal. Calc. for  $\text{C}_{25}\text{H}_{36}\text{O}_5$ : C, 72.08; H, 8.71. Found: C, 71.99; H, 8.68.

(b) To a solution of 2 g of 3 $\alpha$ -acetoxy-11,20-dioxopregnane (VI) in 30 cc of carbon tetrachloride were added 10 cc of acetic anhydride and 0.4 cc of 50% perchloric acid. The mixture was stirred for 1.5 hours at room temperature and the resulting solution was diluted with dichloromethane and was washed with cold sodium bicarbonate solution and with water. After drying, the solvent was removed and the resulting amorphous product (2.605 g) was chromatographed on 75 g of aluminum oxide (pH 6-6.5). Petroleum ether - benzene (1:1) eluted 1 g of crystalline VII, m.p. 125-126°, identical with the product described under (a). The following fractions (150 mg) were amorphous. Petroleum ether - benzene (1:4) eluted 300 mg of a second crystalline substance, m.p. 126-130°, depressed upon admixture of both VI and VII;  $\nu_{\text{max}}^{\text{CHCl}_3}$  1258  $\text{cm}^{-1}$  (acetate), 1715  $\text{cm}^{-1}$  (11-ketone), 1730 and 1735  $\text{cm}^{-1}$  (3 $\alpha$ - and 20-acetates). The crude crystalline product which gave a positive tetranitromethane reaction was analyzed for its acetyl contents. Anal. Calc. for  $\text{C}_{25}\text{H}_{36}\text{O}_5$ :  $\text{CH}_3\text{CO}$ , 20.67. Found:  $\text{CH}_3\text{CO}$ , 17.87. We considered this product to be the geometric isomer of VII and proved its structure by the following reaction. To a solution of 277 mg of this substance in 10 cc of carbon tetrachloride was added 90 mg of N-bromosuccinimide and the mixture was refluxed over a photoflood lamp for 10 minutes. The usual working up afforded 271 mg of a yellow oil which gave, upon filtration through 10 g of silica gel, 200 mg of crystalline  $\Delta^{16}$ -3 $\alpha$ -acetoxy-11,20-dioxopregnene, m.p. 149-152°, not depressed upon admixture of an authentic sample; the infrared spectrum of the product was identical with that of an authentic sample. The formation of the  $\Delta^{16}$ -20-ketone in the reaction confirms that the second crystalline product isolated from the enol acetylation reaction was the geometric isomer of VII.<sup>14</sup>

The benzene-ether-methanol fractions of the original chromatogram consisted of 420 mg of starting material VI. Considering the recovery of starting material, the yield of the enol acetates was 83%.

#### 17 $\alpha$ -Chloro-3 $\alpha$ -acetoxy-11,20-dioxopregnane (VIII)

##### (a) From the 11,20-Diketone VI

To a solution of 2 g of 3 $\alpha$ -acetoxy-11,20-dioxopregnane (VI) in 20 cc of acetic acid was added, dropwise and with stirring, 52.2 cc of a 0.205 *N* solution of chlorine in acetic acid. The mixture was stirred for another 10 minutes and poured into ice water. The precipitate was filtered, washed to neutral, and dried. The colorless solid (2.05 g), m.p. 80-95°, was recrystallized from ether and thus gave 60 mg of a chlorinated product, m.p. 152-160°,  $[\alpha]_D^{26} +72.6^\circ$  ( $c$ , 1.0 in  $\text{CHCl}_3$ ), representing probably the 17,21-dichloride.

The mother liquors of this crystallization were chromatographed on 60 g of aluminum oxide (pH 7). Petroleum ether - benzene (1:1) eluted 450 mg (20%) of monochloride VIII, m.p. 130-142°. After one recrystallization from ether, the product melted at 141-144°.

<sup>14</sup>Compare reference 37.



$[\alpha]_D^{26} + 25.4^\circ$  (c, 1.1 in  $\text{CHCl}_3$ ). The melting point was not depressed upon admixture with authentic VIII (see below); the infrared spectra of the two samples were identical.

Benzene-ether (4:1) eluted 320 mg of crude crystalline  $\Delta^{16}$ -3 $\alpha$ -acetoxy-11,20-dioxopregnene, identified by its infrared spectrum and mixed melting point with an authentic sample. The ethyl acetate fractions gave 270 mg of crystalline  $\Delta^{16}$ -3 $\alpha$ -hydroxy-11,20-dioxopregnene, m.p. 180–195°, identified by infrared comparison and mixed melting point with an authentic sample.

(b) *From the Enol Diacetate VIII*

To a solution of 1.45 g of  $\Delta^{17(20)}$ -3 $\alpha$ ,20-diacetoxy-11-oxopregnene (VII), m.p. 102–117°, in 60 cc of acetic acid was added, at room temperature, dropwise and with stirring, 38.5 cc of a 0.183 *N* solution of chlorine in acetic acid. The colorless mixture was poured into ice water, and the precipitate was filtered, washed to neutral, and dried. The product (1.401 g) was recrystallized from ether and gave 1.2 g of monochloride VIII, m.p. 137–140° (84% yield). The melting point was raised upon one recrystallization to 147–149°. A sample was recrystallized once for analysis: needles, m.p. 150–151°,  $[\alpha]_D^{26} + 20.5^\circ$  (c, 1.02 in  $\text{CHCl}_3$ ),  $\nu_{\text{max}}^{\text{KBr}}$  1245  $\text{cm}^{-1}$  (acetate), 1708  $\text{cm}^{-1}$  (11-ketone), 1735  $\text{cm}^{-1}$  (broad band) (acetate and 20-ketone). Anal. Calc. for  $\text{C}_{23}\text{H}_{33}\text{O}_4\text{Cl}$ : C, 67.55; H, 8.13; Cl, 8.67. Found: C, 67.22; H, 8.00; Cl, 8.59.

*21-Bromo-17 $\alpha$ -chloro-3 $\alpha$ -acetoxy-11,20-dioxopregnane (XIa)*

A solution of 650 mg of 17 $\alpha$ -chloro-3 $\alpha$ -acetoxy-11,20-dioxopregnane (VIII), m.p. 147–149°, in 10 cc of acetic acid, containing 2 cc of a 20% hydrogen bromide solution in acetic acid, was heated to 60°. To this mixture, a solution of 255 mg of bromine in 16 cc of acetic acid was added, dropwise and with stirring, in the course of 15 minutes. Subsequently, the almost colorless solution was poured into ice water, the precipitate was filtered, washed to neutral, and dried. The resulting colorless product (822 mg) was recrystallized from ether to give 490 mg (63% yield) of bromide XIa, m.p. 170–174°. A sample was recrystallized three times for analysis: needles, m.p. 183–184°,  $[\alpha]_D^{26} + 35^\circ$  (c, 0.411 in  $\text{CHCl}_3$ ),  $\nu_{\text{max}}^{\text{KBr}}$  1260  $\text{cm}^{-1}$  (acetate), 1700  $\text{cm}^{-1}$  (11-ketone), 1718  $\text{cm}^{-1}$  (broad band) (21-bromo-20-ketone and acetate). Anal. Calc. for  $\text{C}_{23}\text{H}_{32}\text{O}_4\text{BrCl}$ : C, 56.62; H, 6.61; Br, 16.38; Cl, 7.27. Found: C, 56.62; H, 6.84; Br, 16.28; Cl, 7.26.

*21-Bromo-17 $\alpha$ -chloro-3 $\alpha$ -hydroxy-11,20-dioxopregnane (XI)*

A quantity of 460 mg of 21-bromo-17 $\alpha$ -chloro-3 $\alpha$ -acetoxy-11,20-dioxopregnane (XIa), m.p. 170–174°, was suspended in a solution of 1 cc of 70% perchloric acid in 39 cc of methanol. The mixture was shaken for 22 hours at room temperature. During that time the product dissolved gradually. Subsequently, the solution was poured into an ice-cold sodium bicarbonate solution and the precipitate was extracted with dichloromethane. The organic solution was washed with water and dried over sodium sulphate. The solvent was removed *in vacuo* and the colorless residue (420 mg) was crystallized from ether. There was obtained 285 mg of small prisms, m.p. 160–162°. A sample was recrystallized twice from ether-acetone-hexane for analysis: m.p. 167–169°,  $[\alpha]_D^{26} + 20.4^\circ$  (c, 0.756 in  $\text{CHCl}_3$ ),  $\nu_{\text{max}}^{\text{KBr}}$  1698  $\text{cm}^{-1}$  (11-ketone), 1721  $\text{cm}^{-1}$  (21-bromo-20-ketone), 3450  $\text{cm}^{-1}$  (hydroxy). Anal. Calc. for  $\text{C}_{21}\text{H}_{30}\text{O}_3\text{BrCl}$ : C, 56.57; H, 6.78; Br, 17.92; Cl, 7.95. Found: C, 56.80; H, 6.56; Br, 17.88; Cl, 7.65.

*17 $\alpha$ -Chloro-21-acetoxy-3 $\alpha$ -hydroxy-11,20-dioxopregnane (IX)*

A mixture of 3.683 g of 21-bromo-17 $\alpha$ -chloro-3 $\alpha$ -hydroxy-11,20-dioxopregnane (XI), m.p. 150–152°, 100 mg of potassium iodide, and 7.4 g of freshly fused potassium acetate

was refluxed in 200 cc of absolute acetone and 10 cc of acetic acid for 22 hours in a nitrogen atmosphere. The product was diluted with methylene chloride, and the organic solution was washed with cold sodium bicarbonate solution and with water and was dried over sodium sulphate. Removal of the solvent afforded 3.616 g of a foamish material which crystallized from ether. One recrystallization gave 1.08 g of slightly yellowish prisms, m.p. 160–170° decomp. A sample was recrystallized twice from ethyl acetate – ether for analysis: m.p. 188° decomp.,  $[\alpha]_D^{26} +12^\circ$  (c, 1.0 in  $\text{CHCl}_3$ ),  $\nu_{\text{max}}^{\text{KBr}}$  1230  $\text{cm}^{-1}$  (acetate), 1705  $\text{cm}^{-1}$  (11-ketone), 1725 and 1750  $\text{cm}^{-1}$  (21-acetoxy-20-keto doublet), 3400  $\text{cm}^{-1}$  (hydroxy). Anal. Calc. for  $\text{C}_{23}\text{H}_{33}\text{O}_5\text{Cl}$ : C, 65.00; H, 7.83; Cl, 8.35. Found: C, 65.02; H, 8.05; Cl, 8.35.

The mother liquors of the first crystallization were chromatographed on 200 g of silica gel. Benzene – ethyl acetate (87:13) eluted 687 mg of IX, m.p. 177–179° decomp. (total yield 50%).

*17 $\alpha$ -Chloro-21-acetoxy-3,11,20-trioxopregnane (XII)*

To a stirred solution of 982 mg of 17 $\alpha$ -chloro-21-acetoxy-3 $\alpha$ -hydroxy-11,20-dioxopregnane (IX), m.p. 177–179° decomp., in 50 cc of absolute acetone was added, dropwise, at 0–5°, 1.6 cc of an oxidizing solution prepared by dissolving 267 mg of chromic acid in 230 cc of concentrated sulphuric acid and 770 cc of water. After 2.5 minutes the solution was poured into water and the precipitate was filtered, washed, and dried. The product (977 mg) was recrystallized from ether to give 888 mg (90% yield) of colorless needles, m.p. 184–185° decomp. A sample was recrystallized twice from acetone–hexane for analysis: m.p. 203.5–205.5° decomp.,  $[\alpha]_D^{26} +15^\circ$  (c, 1.01 in  $\text{CHCl}_3$ ),  $\nu_{\text{max}}^{\text{KBr}}$  1708  $\text{cm}^{-1}$  (double band of 3- and 11-ketones), 1740  $\text{cm}^{-1}$  (shoulder) (21-acetoxy-20-ketone), 1765  $\text{cm}^{-1}$  (20-keto-21-acetate).

*$\Delta^4$ -17 $\alpha$ -Chloro-21-acetoxy-3,11,20-trioxopregnene (XVIa)*

To a solution of 439 mg of 17 $\alpha$ -chloro-21-acetoxy-3,11,20-trioxopregnane (XII), m.p. 201–202° decomp., in 25 cc of acetic acid were added, dropwise and with stirring, 0.1 cc of a 15% hydrogen bromide solution in acetic acid and subsequently 2.18 cc of a 0.96 *N* bromine solution in acetic acid. Some of the reaction product crystallized from the mixture towards the end of the addition. The mixture was poured into ice water and the precipitate was filtered, washed, and dried. The resulting crude bromide (522 mg) gave, upon one recrystallization from methylene chloride – hexane, 334 mg of pure 4 $\beta$ -bromo-17 $\alpha$ -chloro-21-acetoxy-3,11,20-trioxopregnane (XIII), m.p. 190–191° decomp. The mother liquors yielded a second crop of 83 mg of the same substance of lesser purity, m.p. 180–182° decomp. (total yield 80%),  $\nu_{\text{max}}^{\text{KBr}}$  1240  $\text{cm}^{-1}$  (acetate), 1708  $\text{cm}^{-1}$  (double band of 3- and 11-ketones), 1735 and 1762  $\text{cm}^{-1}$  (21-acetoxy-20-keto doublet).

A portion of the pure bromo chloride (XIII) (322 mg, m.p. 190–192° decomp.) was dissolved in 60 cc of dichloromethane and 40 cc of *t*-butyl alcohol and treated in the usual manner (26), during 120 minutes, with 96 mg of semicarbazide base in a carbon dioxide atmosphere. The product was taken to dryness *in vacuo* and further dried by azeotropic distillation with benzene. The residue was slurried with a small amount of aqueous ethanol and the mixture was poured into 500 cc of water. The precipitate was filtered, washed, and dried. There was obtained 283 mg (83% yield from XIII) of colorless  $\Delta^4$ -17 $\alpha$ -chloro-21-acetoxy-3,11,20-trioxopregnene-3-semicarbazone, (XIV), m.p. 210° decomp.,  $\lambda_{\text{max}}^{\text{EtOH}}$  270  $\mu$  (log  $\epsilon$  4.3).

A quantity of 280 mg of semicarbazone (XIV) was dissolved in 14 cc of acetic acid and 4 cc of water. The solution was flushed with carbon dioxide and 0.72 cc of a 1.62 *N*

pyruvic acid solution was added. The mixture was stirred and kept for 18 hours at room temperature under carbon dioxide. The usual working up gave 274 mg of crude crystalline  $\Delta^4$ -17 $\alpha$ -chloro-21-acetoxy-3,11,20-trioxopregnene (XVIa). One crystallization from ether gave 183 mg (74% yield from XIV) of pure 17 $\alpha$ -chloro-11-dehydrocorticosterone acetate (XVIa), m.p. 131–132°. A sample was recrystallized twice from ether for analysis: colorless needles, m.p. 137–138°,  $[\alpha]_D^{26} +105^\circ$  (*c*, 0.75 in  $\text{CHCl}_3$ ),  $\lambda_{\text{max}}^{\text{EtOH}}$  238  $\mu$  ( $\log \epsilon$  4.2),  $\nu_{\text{max}}^{\text{KBr}}$  1238  $\text{cm}^{-1}$  (acetate), 1625 and 1680  $\text{cm}^{-1}$  ( $\Delta^4$ -3-keto doublet), 1709  $\text{cm}^{-1}$  (11-ketone), 1738 and 1762  $\text{cm}^{-1}$  (21-acetoxy-20-keto doublet). Anal. Calc. for  $\text{C}_{23}\text{H}_{29}\text{O}_5\text{Cl}$ : C, 65.63; H, 6.95; Cl, 8.42. Found: C, 65.58; H, 7.25; Cl, 8.40.

$\Delta^4$ -17 $\alpha$ -Chloro-21-hydroxy-3,11,20-trioxopregnene (XVI)

A quantity of 150 mg of 17 $\alpha$ -chloro-11-dehydrocorticosterone acetate (XVIa), m.p. 133–135°, was dissolved in a mixture of 9.8 cc of methanol and 0.25 cc of 70% perchloric acid. The solution was stored in a carbon dioxide atmosphere for 22 hours. Subsequently, the product was taken up in dichloromethane and the solution was washed with cold sodium bicarbonate solution and with water and was dried over sodium sulphate. Removal of the solvent *in vacuo* gave 148 mg of an amorphous product which crystallized from acetone–hexane. One crystallization afforded 120 mg of 17 $\alpha$ -chloro-11-dehydrocorticosterone (XVI), m.p. 104° decomp. A sample was recrystallized twice from acetone–hexane for analysis: fine needles, m.p. 107° decomp.,  $[\alpha]_D^{26} +141^\circ$  (*c*, 0.733 in  $\text{CHCl}_3$ ),  $\lambda_{\text{max}}^{\text{EtOH}}$  238  $\mu$  ( $\log \epsilon$  4.1),  $\nu_{\text{max}}^{\text{KBr}}$  1620 and 1675  $\text{cm}^{-1}$  ( $\Delta^4$ -3-keto doublet), 1708  $\text{cm}^{-1}$  (double band of 11- and 20-ketones), 3450  $\text{cm}^{-1}$  (21-hydroxy). Anal. Calc. for  $\text{C}_{23}\text{H}_{27}\text{O}_4\text{Cl}$ : C, 66.57; H, 7.18; Cl, 9.36. Found: C, 66.68; H, 7.43; Cl, 9.42.

Acetylation

To a solution of 95 mg of ketol XVI, m.p. 90–100° decomp., in 4 cc of pyridine, 0.5 cc of acetic anhydride was added. The mixture was kept overnight at room temperature and worked up in the usual fashion. There was obtained 96 mg of a colorless foam which crystallized upon trituration with ether, m.p. 131–132°. The melting point was not depressed upon admixture with authentic acetate XVIa and the infrared spectrum of the product was identical with that of an authentic sample prepared as described above.

$\Delta^4$ -16-21-Acetoxy-3,11,20-trioxopregnadiene (XV)

To a solution of 91 mg of 17 $\alpha$ -chloro-11-dehydrocorticosterone acetate (XVIa), m.p. 132–133°, in 5 cc of dimethylformamide, was added 10 mg of potassium iodide and the mixture was refluxed for 2 hours in a nitrogen atmosphere. After cooling, 0.5 cc of acetic anhydride was added and the reaction mixture was stored at room temperature for 20 hours. The usual working up gave 89 mg of a brown oil which was chromatographed on 3 g of aluminum oxide. Benzene eluted 17 mg of starting material, m.p. 135–136°, and benzene–ether mixtures eluted 10 mg of the diene XV, identified by mixed melting point and by infrared comparison with an authentic sample (compare reference 22 and footnote 9).

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## SOLID-LIQUID REACTIONS

### PART I. THE DETERMINATION OF SOLID-LIQUID REACTION MECHANISMS<sup>1</sup>

ROGER KELLY<sup>2</sup>

#### ABSTRACT

A tracer method has been described by Graham, Spinks, and Thorvaldson for investigating the mechanisms of solid-liquid reactions. The present work represents an attempt to develop the theory of this method in detail and thereby allow for a greater variety of experimental conditions. Thus, no restrictions are placed on the compositions of the reacting and product solids, nor on the initial location of the tracer. The effect of exchange between the liquid and both solids is taken into account. Furthermore, two different *systems* of mechanisms are considered. In the one, which is shown to be the more realistic when rapid, multidirectional "external" exchange is present, mechanisms are classified according to whether or not the reaction proceeds at the surfaces of the solids; in the other, applicable in the absence of "external" exchange or when the exchange is slow, mechanisms are classified according to the degree of mixing with the liquid of successively reacting portions of the reacting solid.

#### INTRODUCTION

A solid-liquid reaction may be defined as one in which a solid of low solubility (the reacting solid) reacts with a liquid to form a second solid of even lower solubility (the product solid), the term liquid being here intended to include both solvent and solute indiscriminately. Reactions of this kind are of particular interest in cement chemistry, since they are responsible for both the setting and deterioration of cementitious substances (2). Specific examples include the hydrations of the calcium silicates (1),  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (3), and  $\text{CaO}$  (4); the conversion of insoluble sulphates to carbonates (5, p. 585); and the reactions described in reference 6.

Innumerable variations in the details of solid-liquid reaction mechanisms are undoubtedly possible; however, the mechanisms will tend to fall into general classes or *systems* which represent to first approximation the limits of experimental distinguishability. One such system, much used in past work (1, 3, 4), considers the *degree of mixing* with the liquid of successively reacting portions of the reacting solid (Fig. 1A). Thus, in a "through-solution" mechanism the reacting solid passes into solution before precipitating as product solid (7). In a "direct" mechanism, on the other hand, the reacting solid is converted to the product solid without an intermediate mixing with the body of the liquid; the liquid is, however, assumed to receive or supply material as required by the balanced reaction equation (3, 4). Depending on the relative ease of the "through-solution" and "direct" routes, mixed mechanisms might also occur.

A possible alternative to the above system of mechanisms considers whether or not the reaction proceeds at the surfaces of the solids (Fig. 1B). In a "surface" mechanism material is transferred from the surface of the reacting solid to that of the product solid, with or without mixing with the body of the liquid. In an "internal" mechanism reaction proceeds as a result of liquid diffusing, or otherwise penetrating, into the interior of the reacting solid. The reaction thus occurs *without* mixing, and the product solid is

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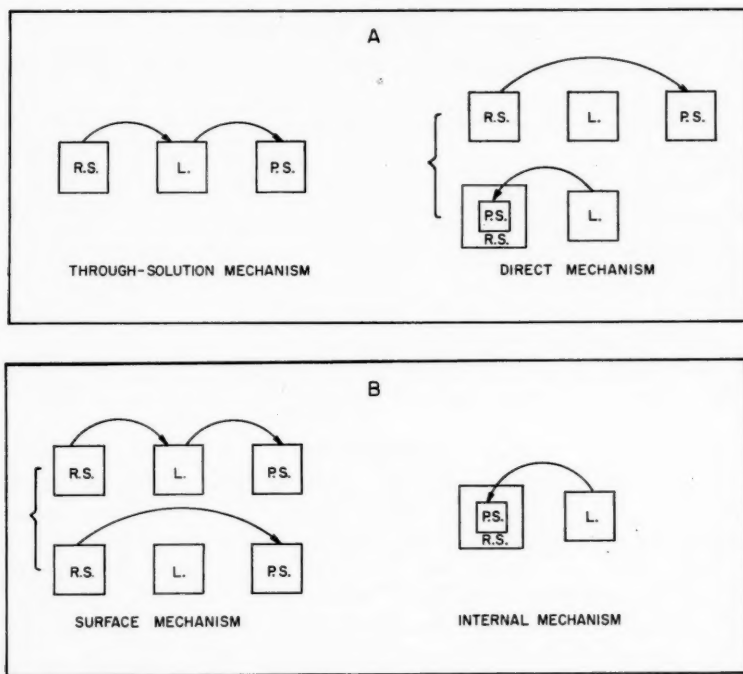


FIG. 1. (A) Schematic representation of solid-liquid reaction mechanisms as classified according to the degree of mixing with the liquid of successively reacting portions of the reacting solid. The following abbreviations are used: R.S. = reacting solid, L. = liquid, P.S. = product solid. The arrows may in general be interpreted as the routes taken by material from the reacting solid and liquid during the course of the reaction; however, it has been necessary to leave out certain steps in which differences in composition between the reacting and product solids are made up by the liquid, since the details of these steps depend on the actual compositions of the solids.

(B) Schematic representation of solid-liquid reaction mechanisms as classified according to whether or not the reaction proceeds at the surfaces of the solids. Abbreviations and use of arrows are as in (A).

deposited within the reacting solid, out of contact with the liquid (cf. the hydration of soft-burnt CaO (4)). Mixed mechanisms would again be possible.

Perhaps the most powerful method for investigating solid-liquid reaction mechanisms within either system is the tracer method of Graham, Spinks, and Thorvaldson (1). A suitable label, which will be assumed here to be a radioactive nuclide, is introduced into the liquid or reacting solid or both. The reaction is then allowed to proceed under conditions of vigorous agitation, and concurrent measurements of radioactivity and composition are made on the *filtered* liquid at suitable time intervals. A different relation between these measured quantities exists for each mechanism within a given system, *provided the system is applicable*.

The remainder of the present work will be concerned with a detailed treatment, in the light of the two systems of mechanisms just described, of the problem of correlating the activity and composition of the liquid during labeled solid-liquid reactions. This will lead to a precise definition of the conditions under which a given system of mechanisms is physically realistic, and will also provide a set of general equations with which to interpret



experimental results.<sup>3</sup> It will be assumed, in all cases, that the reaction mixture is subjected to sufficient agitation to maintain a uniform composition in the liquid.

#### SOLID-LIQUID REACTIONS ACCOMPANIED BY EXTERNAL EXCHANGE

In any attempt to correlate the activity and composition of the liquid in labeled solid-liquid reactions, close attention must be given to the effect of exchange between the liquid and both solids. Such exchange has been recognized to be of three extreme types (8, p. 37): surface exchange, self-diffusion, and recrystallization. Closely related to recrystallization is the formation of solid intermediates. For the present purposes, however, a slightly different systematization will be used:

(i) "external" exchange: exchange which occurs between a liquid and ions located in the *outer* layers of a solid, and which proceeds irrespective of crystallographic differences between the ions of the solid. Surface exchange and recrystallization are probably always of this sort.

(ii) "internal" exchange: exchange occurring between a liquid and a crystallographically determined fraction of a solid and thence, when rapid, occurring throughout the entire relevant portion of the crystal lattice. Self-diffusion may be of this sort in particular cases, for example compounds with a defect structure (9, 10).

Consider first a reaction accompanied by rapid, multidirectional external exchange *in one or both* solids, with or without a component of similar internal exchange in addition. (By rapid is meant having a rate greater than the rate of reaction, while multidirectional is the opposite of unidirectional (cf. 8, p. 35).) The result of such exchange is that the surfaces of the affected solids tend to have the same specific activity as the liquid. Accordingly, if the reaction proceeds at the surfaces, the material undergoing reaction is always in radioactive equilibrium with the liquid *whatever the degree of mixing*. Mechanisms based on the degree of mixing are therefore not experimentally significant, and the reaction is more readily described in terms of "surface" and "internal" mechanisms (cf. Fig. 1B).

##### (a) Surface Mechanism

Let  $a$  be the amount of labeled species with specific activity  $f(0)$  initially present in the liquid. Let  $b$  be the amount of labeled species with specific activity  $g$  initially present in the reacting solid,  $x$  being the portion of  $b$  which has reacted. For  $x > 0$  the specific activity of the liquid is then  $f(x)$ . Let  $m_1$  and  $m_2$  be the numbers of moles of labeled species in the formulae of, respectively, the reacting and product solids as derived from the balanced reaction equation.<sup>4</sup> Let  $n_1$  and  $n_2$  be such portions of, respectively,  $m_1$  and  $m_2$  that the total amount of rapidly and multidirectionally exchanging material, whether external or internal, in a given solid can be represented as a fraction  $n_i/m_i$  of the total amount of solid. This material has specific activity  $f(x)$ . (In a more rigorous treatment, the amount of *externally* exchanging material would be put proportional to the surface area of the solid, i.e. to  $(\text{amount})^{2/3}$ .)

In accordance with this nomenclature, a "surface" mechanism can be envisaged as involving the reaction of successive elements of material,  $\Delta x$ , from the surface of the reacting solid, together with corresponding changes in activity. The latter are as follows:  $\Delta x f(x)$  leaves the reacting solid,  $(1 - n_1/m_1)\Delta x g$  becomes exchangeable beneath the

<sup>3</sup>Equations applicable in certain specific cases have already been given by Thorvaldson et al. (1, 3).

<sup>4</sup>For example, in the reaction  $2(3\text{CaO} \cdot \text{SiO}_2) + (n+3)\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot n\text{H}_2\text{O} + 3\text{Ca}^{++} + 6\text{OH}^-$ ,  $m_1 = 6$  and  $m_2 = 3$  if calcium is labeled (cf. 1).

surface of the reacting solid,<sup>5</sup>  $(m_2/m_1)\Delta x f(x)$  deposits on the product solid,  $(1-n_2/m_2)(m_2/m_1)\Delta x f(x)$  ceases to be exchangeable beneath the surface of the product solid,<sup>5</sup> and the liquid gains  $(1-m_2/m_1)\Delta x f(x)$ . The specific activity of the liquid and the exchanging portions of the solids therefore changes from  $f(x)$  to

$$f(x+\Delta x) = (\text{total mobile activity})/(\text{total mobile amount})$$

$$= \frac{\left[ a + \left(1 - \frac{m_2}{m_1}\right)(x+\Delta x) \right] f(x) + \left[ \frac{n_1}{m_1} (b-x)f(x) - \Delta x f(x) + \left(1 - \frac{n_1}{m_1}\right) \Delta x g \right] + \left[ \frac{n_2}{m_1} x + \frac{m_2}{m_1} \Delta x - \left(1 - \frac{n_2}{m_2}\right) \frac{m_2}{m_1} \Delta x \right] f(x)}{\left[ a + \left(1 - \frac{m_2}{m_1}\right)(x+\Delta x) \right] + \left[ \frac{n_1}{m_1} (b-x) - \Delta x + \left(1 - \frac{n_1}{m_1}\right) \Delta x \right] + \left[ \frac{n_2}{m_1} x + \frac{m_2}{m_1} \Delta x - \left(1 - \frac{n_2}{m_2}\right) \frac{m_2}{m_1} \Delta x \right]}$$

If  $[f(x+\Delta x)-f(x)]/\Delta x$  is now formed,  $df(x)/dx$  can be obtained in the limit as  $\Delta x \rightarrow 0$ . Integrating the latter expression under the condition that

$$f(x) = \frac{af(0) + n_1 bg/m_1}{a + n_1 b/m_1}$$

when  $x = 0$ , i.e. allowing for the initial "burst" of exchange, the result is

$$[1] \quad f(x) = g + \frac{f(0) - g}{1 + n_1 b/m_1 a} \left( 1 + \frac{m_1 - m_2 - n_1 + n_2}{m_1 a + n_1 b} x \right)^{(-m_1 + n_1)/(m_1 - m_2 - n_1 + n_2)}$$

The activity of the liquid as a function of  $x$  follows directly from equation [1]:

$$[2] \quad \text{activity} = (a + x - m_2 x/m_1) f(x) \equiv Af(x),$$

or, in units of fraction of total activity present,

$$[3] \quad \text{fractional activity} = \frac{Af(x)}{af(0) + bg}.$$

The term

$$[4] \quad A \equiv a + x - m_2 x/m_1$$

represents the measured amount of labeled species present in the liquid at any stage of reaction; that is, it is simply the "composition" of the liquid.

In those cases where the activity is confined initially to either the liquid or solid, and  $n_1 = n_2 = 0$ , equations [1] to [3] simplify considerably, the last designated giving

$$[5] \quad \begin{cases} g = 0, & m_1 \neq m_2 \\ g = 0, & m_1 = m_2 \end{cases} \quad \text{fractional activity} = \frac{(A/a)^{m_2/(m_2-m_1)}}{e^{-x/a}}$$

<sup>5</sup>The origin of the factors  $(1-n_1/m_1)$  and  $(1-n_2/m_2)$  is as follows. Let  $n_i'$  and  $n_i''$  correspond, respectively, to externally and internally exchanging material. Then the removal or deposition in the course of reaction of  $\Delta x$  units of material at the outside of the surface layer described by  $n_i'$  will cause an amount on the inner side of this layer to become, or cease to be, exchangeable which is given by  $\Delta x$  times a factor  $(1-n_i'/m_i)$  to take into account the reduced amount of material inside the layer, times a factor  $(1-n_i''/m_i)$  since only part of the new material is not already exchanging. Noting that  $n_i = n_i' + n_i'' - n_i' n_i''/m_i$ , it follows that the total amount of material becoming, or ceasing to be, exchangeable is  $(1-n_i/m_i)\Delta x$ .

$$[6] \quad \begin{cases} f(0) = 0, & m_1 \neq m_2 \\ f(0) = 0, & m_1 = m_2 \end{cases} \quad \begin{aligned} \text{fractional activity} &= A/b - \frac{a}{b} (A/a)^{m_2/(m_2-m_1)} \\ &= \frac{a}{b} (1 - e^{-x/a}). \end{aligned}$$

If the reacting solid suffers total exchangeability, i.e.  $n_1 \rightarrow m_1$ , the reductions of equations [1] and [3] are, respectively,

$$[7] \quad f(x) = \frac{af(0)+bg}{a+b} \quad \text{and} \quad \text{fractional activity} = \frac{A}{a+b}.$$

These expressions are seen to describe radioactive equilibrium. The case  $n_2 \rightarrow m_2$  is equivalent to the occurrence of extensive recrystallization in the product solid, which is discussed later. If the exchange is slow or unidirectional, though such that the outer surfaces of at least one solid maintain radioactive equilibrium with the liquid, the activity will be bounded by that obtained with full values of  $n_1$  and  $n_2$ , and that obtained with  $n_1 = n_2 \rightarrow 0$ .

An equation somewhat different from [1] is obtained when  $m_2$  is not a constant but a function of  $A$ : see Appendix.

#### (b) Internal or Mixed Mechanism

The derivation of an equation analogous to [1] for cases in which either a purely "internal" mechanism, or a mixture of "surface" and "internal" mechanisms, occurs is complicated by the fact that the product solid, either completely or in part, is now lodged inaccessibly within the reacting solid and contributes to the exchangeability of the system only as the reacting solid is depleted.<sup>6</sup> It will therefore be assumed for the present that  $n_2 \rightarrow 0$ , the case  $n_2 \rightarrow m_2$  being covered in the subsequent discussion of recrystallization. The elemental activity changes occurring as a result of the reaction of  $\Delta x$  units of material from the reacting solid,  $k\Delta x$  of which is from a surface and  $(1-k)\Delta x$  from the interior, are then as follows:  $k\Delta x f(x)$  leaves the surface of the reacting solid,  $k(1-n_1/m_1)\Delta x g$  becomes exchangeable beneath the surface of the reacting solid,<sup>5</sup> and the liquid gains

$$\begin{aligned} &\left(1 - \frac{m_2}{m_1}\right) \Delta x f(x) && \text{if } m_1 < m_2, \\ &k\left(1 - \frac{m_2}{m_1}\right) \Delta x f(x) + (1-k)\left(1 - \frac{m_2}{m_1}\right) \Delta x \left(\frac{n_1}{m_1} f(x) + \left(1 - \frac{n_1}{m_1}\right) g\right) && \text{if } m_1 > m_2. \end{aligned}$$

In the latter expression, the term beginning with  $(1-k)$  is strictly valid only if soluble reaction products formed in the interior of the reacting solid as a result of the "internal" component of the reaction are able to diffuse out rapidly. Following through the derivation, two expressions for  $f(x)$  are finally obtained:

$$[8] \quad m_1 < m_2 \quad f(x) = g + \frac{f(0)-g}{1+n_1b/m_1a} \left(1 + \frac{m_1-m_2-n_1}{m_1a+n_1b} x\right)^{-k(m_1-n_1)/(m_1-m_2-n_1)}$$

$$[9] \quad m_1 > m_2 \quad f(x) = g + \frac{f(0)-g}{1+n_1b/m_1a} \left(\dots\right)^{[-k(m_1-n_1)(1-k)\left(1-\frac{m_2}{m_1}\right)(m_1-n_1)]/(m_1-m_2-n_1)}$$

<sup>6</sup>It has been assumed, both here and in the initial description of the "internal" mechanism (see Introduction), that that portion of the product solid laid down within the reacting solid remains inaccessible to the liquid until the covering layer of reacting solid has disappeared. Actually, it is conceivable that in some cases the liquid might have continuous access to the internal product solid. The reaction would then show an "internal" mechanism only if the external exchange exhibited by the product solid were slow or non-existent; otherwise the reaction would follow a "surface" mechanism.

Hence, if  $n_1 \rightarrow 0$ ,

$$[10] \quad \begin{cases} g = 0, & m_1 < m_2 & \text{fractional activity} = (A/a)^{[m_2 - (1-k)m_1]/(m_2 - m_1)} \\ g = 0, & m_1 = m_2 & = e^{-kx/a} \\ g = 0, & m_1 > m_2 & = (A/a)^{-km_2/(m_1 - m_2)} \end{cases}$$

$$[11] \quad f(0) = 0 \quad \text{like equations [6] but with exponents as above.}$$

#### SOLID-LIQUID REACTIONS ACCOMPANIED BY INTERNAL OR NO EXCHANGE

If the external exchange is either slow or non-existent in both solids, though without restriction to the internal exchange, a distinction between "surface" and "internal" mechanisms is no longer experimentally convenient. Different *degrees of mixing* (cf. Fig. 1A) are, however, readily distinguished. It can be shown that, since the "through-solution" mechanism results in a complete mixing with the liquid of successively reacting portions of the reacting solid, the relation between the activity and composition of the liquid for this mechanism is identical with that for a "surface" mechanism: see equations [1], [5], [6], and [16], the last designated applying when  $m_2$  is a function of  $A$ . Similarly, for a "direct" or mixed mechanism the activity is given by equations [8] to [11].

Previously studied solid-liquid reactions were described as following mechanisms based on the degree of mixing (1, 3, 4). There is reason to believe, however, that the product solids in at least two of the reactions (the hydrations of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (3) and  $\text{CaO}$  (4)) exhibit rapid, multidirectional external exchange.<sup>7</sup> The reactions in question are therefore perhaps better represented in terms of "surface" or "internal" mechanisms; passage through solution may still have occurred, but was not rigorously demonstrated.

#### RECRYSTALLIZATION AND INTERMEDIATE FORMATION

The possibility that extensive recrystallization will take place in the freshly formed product solid, or that solid-intermediate formation will occur, is always a problem in studying a solid-liquid reaction, since neither effect can be predicted from the behavior of the product solid in isolation.

Consider first recrystallization. Assume limiting conditions, i.e. (i) that the recrystallization is rapid, complete, and multidirectional, and (ii) that no product solid is lodged inaccessibly within the reacting solid as might occur with an "internal" or "direct" mechanism, a condition which should be well met as the reaction enters its later stages and the amount of unconverted reacting solid diminishes. Then, *regardless of the reaction mechanism*,

$$[12] \quad f(x) = (\text{total mobile activity})/(\text{total mobile amount}) \\ = \frac{af(0) + xg + n_1(b-x)g/m_1}{a + x + n_1(b-x)/m_1}$$

Forms for fractional activity follow readily using equation [3]; in particular, if  $g = 0$  and either  $n_1 \rightarrow 0$  or  $x \rightarrow b$ ,

<sup>7</sup>That is, the product solids in these reactions both exhibit rapid surface exchange, a mode of exchange which may in general be expected to be multidirectional and external. For  $\text{Ca}(\text{OH})_2$ , see reference 4; for  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , compare reference 11, where surface exchange is shown to occur with  $\text{SrSO}_4$ .

$$[13] \quad \text{fractional activity} = \frac{A}{a+x} = \frac{(A/a)(1-m_2/m_1)}{A/a-m_2/m_1}$$

Similar equations can be obtained by letting  $n_2 \rightarrow m_2$  in equation [1]. If the recrystallization is slow, incomplete, or unidirectional, or a portion of the product solid is inaccessible (i.e. if in effect  $n_2 < m_2$ ), the specific activity of the liquid will lie between that given by equation [12] and that for the unperturbed reactions (either equation [1] (with  $n_2 = 0$ ), [8], or [9]).

Solid-intermediate formation will be largely equivalent to recrystallization in the product solid in such cases as (i) "surface" or "through-solution" mechanisms occur, and (ii) the intermediates are reasonably long-lived, i.e. not transient.

Note that equations [12] and [13] were derived without regard to the reaction mechanism; in other words, recrystallization and intermediate formation tend to mask the differences between mechanisms.

#### RELATIVE VALUES OF THE SPECIFIC ACTIVITIES

By way of conclusion, it is interesting to consider the relative values of the specific activities of the liquid to be expected under the various mechanisms after a given extent of reaction, i.e. for a given value of  $x$  or  $A$  (equations [1], [8], and [9]). Exchange will be assumed to be slight, hence  $n_1 = n_2 \rightarrow 0$ ; and mixed mechanisms will be assumed not to occur, hence  $k = 1$  or  $k = 0$ . These specific activities will be compared with the values occurring initially ( $f(0)$ ), at radioactive equilibrium (equations [7]), and when limiting recrystallization or intermediate formation occur (equation [12]). Representing a given specific activity by the appropriate name, one obtains, for  $f(0) > g$ ,

$$[14] \quad \left. \begin{array}{l} \text{(surface or through-solution)} \\ \text{(equilibrium)} \end{array} \right\} < \text{(recrystallization)} < \text{(internal or direct)} < \text{(initial)};$$

except that, for  $m_1 \leq m_2$ , (internal or direct) = (initial), while when the reaction is complete, i.e.  $x \rightarrow b$ , (equilibrium) = (recrystallization). For  $f(0) < g$  the inequalities in equation [14] are reversed. Relative values similar to those in equation [14] also hold for *total* activities, except that the position of the initial activity cannot be predicted simply. The various relationships are further illustrated in Figs. 2A and 2B, where the progress of the specific activity of the liquid is plotted as a function of  $x$  for two particular sets of conditions.

It is seen that only with a "surface" or "through-solution" mechanism does the specific activity of the liquid proceed from its initial value *across* the limiting recrystallization value (or, when  $x \rightarrow b$ , the equilibrium value). Stated differently, the limiting recrystallization and equilibrium activities, whether specific or total, define a boundary between the activities attainable under the different mechanisms of a given system.

An interesting example of the "crossing phenomenon" in a field outside of formal solid-liquid reactions was found by Kolthoff and Eggertsen (12). When fresh  $\text{PbCrO}_4$  was allowed to recrystallize in a solution containing  $\text{Pb}^{212}$ , a transient activity *beyond* the usually encountered equilibrium value was observed. Noting that unidirectional recrystallization is in all respects equivalent to a solid-liquid reaction with  $m_1 = m_2$  which follows a "surface" or "through-solution" mechanism, this observation indicates that the recrystallization was partially unidirectional. A similar conclusion was reached by the authors.

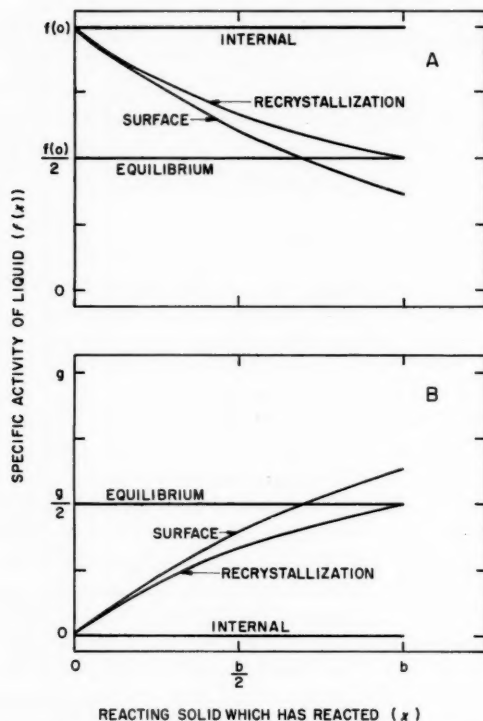


FIG. 2. (A) The progress of the specific activity of the liquid ( $f(x)$ ) during a labeled solid-liquid reaction in which the tracer is confined initially to the liquid ( $g = 0$ ), the numbers of moles of labeled species in the formulae of the reacting and product solids are the same ( $m_1 = m_2$ ; cf. footnote 4), exchange is slight ( $n_1 = n_2 \rightarrow 0$ ), and equal amounts of the labeled species are present initially in the liquid and solid phases ( $a = b$ ). Since  $m_1 = m_2$ , the specific activity is proportional to the total activity. The reaction necessarily terminates when the amount of labeled species from the reacting solid which has reacted ( $x$ ) equals the total amount originally present ( $b$ ).

(B) The progress of the specific activity of the liquid during a labeled solid-liquid reaction under the same conditions as in Fig. 2A except that the tracer is confined initially to the solid ( $f(0) = 0$ ).

#### ACKNOWLEDGMENT

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## APPENDIX

## SOLID-LIQUID REACTIONS WHERE THE COMPOSITION OF THE PRODUCT SOLID VARIES

Suppose, as in the hydration of  $3\text{CaO} \cdot \text{SiO}_2$  (1), that the composition of the product solid depended on the concentration of the liquid. The quantity  $m_2$  could then be expressed as a function of  $A$ ,

$$m_2(A) = c_0 + c_1A + c_2A^2 \dots \approx c_0 + c_1A,$$

where  $c_0$ ,  $c_1$ , and  $c_2$  are constants. Now, in such a case, there is a possibility that that portion of the product solid characterized by  $c_1A$  would not remain inert once precipitated, but (in particular near a surface) would tend to maintain composition equilibrium and thence radioactive equilibrium with the liquid. An external equilibrating shell would therefore occur which, to first approximation, could be envisaged as containing a mole fraction  $h$  of the total variable portion of the product solid, and thence  $hc_1Ax/m_1$  units of material.<sup>8</sup>

Assuming that the reaction follows a "surface" or "through-solution" mechanism, though with  $n_1 = n_2 \rightarrow 0$ , the relation between the activity and composition of the liquid when  $m_2$  is a variable is readily derived. Let  $x$  units of reacting solid already have reacted and another  $\Delta x$  react. The specific activity of the liquid and the equilibrating portion of the product solid therefore changes from  $f(x)$  to

$$(x + \Delta x) = \frac{Af(x) + \Delta xg + (hc_1Ax/m_1)f(x)}{A + \Delta x + hc_1Ax/m_1},$$

where

$$[15] \quad A = a + x - (c_0 + hc_1A)x/m_1 - \int_0^x (1-h)(c_1A/m_1)dx'.$$

Proceeding as before, an expression for  $df(x)/dx$  is obtained. The term  $dx$  can be eliminated by differentiating equation [15], and  $f(x)$  then found by integration. The result, with  $m_2(A)$  substituted for  $(c_0 + c_1A)$ , is

$$[16] \quad f(x) = g + [f(0) - g] \left\{ \frac{[m_1 - m_2(A)]a}{[m_1 - m_2(a)]A} \right\}^{m_1/[m_1 - m_2(0)]}.$$

The activity in the liquid as a function of  $A$  can now be derived as indicated by equations [2] and [3]. Equation [16] is *not* valid if  $m_1 = m_2(0)$  or  $m_2(a)$ , or if  $m_1$  lies within the path of  $m_2(A)$ .

An important property of equation [16] is that, provided it is expressed in terms of  $A$  and not  $x$ , it does not require knowledge of the value of  $h$ , i.e. of the division of product solid into equilibrating and nonequilibrating portions. It can be shown from a more general derivation, in which  $c_1A$  is replaced by  $m_2(A)$  and  $h$  by the generalized form  $h(A)$ , and  $c_0$  is dropped from equation [15], that this result is contingent on the following relation:

$$\frac{dh(A)m_2(A)}{dA} = \frac{h(A)m_2(A)}{A};$$

hence  $h(A)m_2(A) = \text{constant} \cdot A = hc_1A$ . In other words, independence of  $h$  occurs *accidentally* when certain specific conditions are met.

Equation [16] should be of use in determining values of  $m_2(A)$  in cases where the reaction mechanism is not in doubt.

<sup>8</sup>Ideally, the amount of product solid capable of equilibration would be put proportional to the surface area of the product solid; this would, however, introduce an unwieldy two-thirds power.

## SOLID-LIQUID REACTIONS

### PART II. SOLID-LIQUID REACTIONS AMONGST THE CALCIUM ALUMINATES AND SULPHOALUMINATES<sup>1</sup>

ROGER KELLY<sup>2</sup>

#### ABSTRACT

When  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  (i.e.  $\text{C}_3\text{AH}_6$ ) was placed in contact with a solution of  $\text{Ca}(\text{OH})_2$  labeled with  $\text{Ca}^{46}$  and maintained at  $25^\circ\text{C}$ , there was very little change in either the activity or composition of the liquid. These observations, when taken together, indicate that the compound is *probably* stable in the system used. On the other hand, when either  $\text{C}_3\text{AH}_6$  or  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$  (i.e.  $\text{C}_3\text{A}\Sigma\text{H}_{12}$ ) was added to a mixed  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  solution, the composition of the liquid varied in a manner consistent with the formation of  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 31\text{H}_2\text{O}$  (i.e.  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$ ). The activity also changed markedly, and a detailed consideration of the relations between activity and composition enabled the reaction mechanisms to be determined. In further experiments, the reactions of  $\text{C}_3\text{AH}_6$  and  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  to form  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$  were shown to proceed also at  $70^\circ$  and  $90^\circ\text{C}$ . The consistently greater *ultimate* stability of  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$  over  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  between  $25^\circ$  and  $90^\circ\text{C}$  is to be contrasted with the fact, observed in the course of preparing the  $\text{C}_3\text{A}\Sigma\text{H}_{12}$ , that when solutions of  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{CaSO}_4$ , and  $\text{Ca}(\text{OH})_2$  are mixed the *immediate* precipitate is  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$  at room temperature, but  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  at boiling temperature.

*An abbreviated chemical symbolism, similar to the one used by Bogue (1), will be employed in what follows:  $\text{A} \equiv \text{Al}_2\text{O}_3$ ,  $\text{C} \equiv \text{CaO}$ ,  $\text{H} \equiv \text{H}_2\text{O}$ ,  $\Sigma \equiv \text{CaSO}_4$ . Thus  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$  will be represented by  $\text{C}_3\text{A}\Sigma\text{H}_{12}$ .*

Calcium forms four well-defined anhydrous aluminates ( $\text{CA}$ ,  $\text{C}_3\text{A}$ ,  $\text{C}_3\text{A}_5$ , and  $\text{C}_5\text{A}_3$ ) (2) together with perhaps 10 hydrated forms. The most well-known of the latter are  $\text{C}_3\text{AH}_6$  (cubic),  $\text{C}_2\text{AH}_8$ ,  $\text{C}_3\text{AH}_{12}$ , and  $\text{C}_4\text{AH}_{12}$  (all platy hexagonal) (1, p. 552), though there is general agreement that the cubic  $\text{C}_3\text{AH}_6$  is the only stable aluminate in the system  $\text{C}-\text{A}-\text{H}$  between room temperature and  $215^\circ\text{C}$  (3, 4). Representing a further stage of chemical complexity are two long series of insoluble compounds with general formulae  $\text{C}_3\text{AXH}_{12}$  (platy hexagonal) and  $\text{C}_3\text{AX}_3\text{H}_{31}$  (acicular hexagonal), where  $\text{X}$  may be essentially any calcium salt (5). For  $\text{X} = \text{CaSO}_4$  only the acicular form is apparently stable in aqueous systems (6).

These compounds are of importance principally in their relation to portland cement. Thus  $\text{C}_3\text{A}$  is a constituent of the cement powder (it lowers the preparation temperature), while hydrated forms arising from the  $\text{C}_3\text{A}$  are present in set cement. When set cement, as in mortar or concrete, is exposed to sulphate, the hydrated aluminates are converted to the bulky sulphoaluminate  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$  with resultant disintegration of the material.

The present work represents a study of three of the many possible aluminate reactions that might occur in cement: that of  $\text{C}_3\text{AH}_6$  with  $\text{Ca}(\text{OH})_2$  solutions, that of  $\text{C}_3\text{AH}_6$  with mixed  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  solutions, and that of  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  with mixed  $\text{Ca}(\text{OH})_2$ - $\text{CaSO}_4$  solutions. Since these reactions fall into the category of *solid-liquid* reactions (7), they will be considered in terms of the tracer method of Graham, Spinks, and Thorvaldson (8) as extended by Kelly (7).

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## EXPERIMENTAL

*Solutions*

Solutions saturated in  $\text{Ca}(\text{OH})_2$  or  $\text{CaSO}_4$  or both were prepared by shaking for several weeks an excess of the appropriate solid ( $\text{CaO}$  or  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) with redistilled water in glass containers. Less concentrated solutions were made up by dilution. It was attempted at all times to minimize carbonation.

 $\text{C}_3\text{AH}_6$ 

Since wet preparations generally lead to the metastable hexagonal aluminates, a hydrothermal technique due to Thorvaldson and Grace (9) was used to prepare  $\text{C}_3\text{AH}_6$ . Starting with a 3:1 mixture of  $\text{CaO}$  and  $\text{Al}_2\text{O}_3$ ,  $\text{C}_3\text{A}$  was formed by alternately igniting at  $1400^\circ\text{C}$  and grinding to 325 mesh. The  $\text{C}_3\text{A}$  was then converted to  $\text{C}_3\text{AH}_6$  by exposure to the equilibrium vapor pressure of water at  $150^\circ\text{C}$  for 8 days.

 $\text{C}_3\text{A}\Sigma\text{H}_{12}$ 

The only methods for preparing  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  apparently recorded involve precipitations at room temperature from solutions of carefully controlled composition (see, for example, 10). There are, however, isolated examples in which a hexagonal phase resembling  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  has been obtained at elevated temperatures (5). Following the lead of the latter, 150-cc portions of a solution containing 3.06 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  in 1 liter of saturated  $\text{CaSO}_4$  (i.e.  $\text{Al}_2\text{O}_3:\text{SO}_3::1:6$ ) were mixed with 600-cc portions of a  $\text{Ca}(\text{OH})_2$  solution containing about 0.55 g  $\text{CaO}$  per liter, *both solutions being at boiling temperature*. In every instance an immediate precipitate with a striking silky luster and platy hexagonal form was observed (Fig. 1A). Ten minutes at boiling temperature were allowed for crystal growth, if any, before the precipitate was separated. The samples analyzed variously as  $\text{C}_3\text{A}\Sigma_{0.44}\text{H}_{9.7}$ ,  $\text{C}_3\text{A}\Sigma_{0.86}\text{H}_{9.7}$ ,  $\text{C}_3\text{A}(\Sigma_{0.62}\text{C}_{0.46})\text{H}_{10.0}$ , etc., indicating that the desired substance had been obtained, though as a member of a solid-solution series (cf. the series  $\text{C}_3\text{AH}_{12}$ – $\text{C}_3\text{A}\Sigma\text{H}_{12}$ – $\text{C}_4\text{AH}_{12}$  proposed by Kalousek (11)). The deficient water contents probably represent equilibrium compositions at the temperature used.

It was not found possible to prepare *pure*  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  at temperatures below boiling temperature. Thus, when the  $\text{Al}_2(\text{SO}_4)_3$ – $\text{CaSO}_4$  solution described above was mixed with twice the volume of a  $\text{Ca}(\text{OH})_2$  solution containing about 1.1 g  $\text{CaO}$  per liter, mixtures of  $\text{C}_3\text{A}\Sigma\text{H}_{12}$  and  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$  were obtained between  $50^\circ$  and  $75^\circ\text{C}$ , and  $\text{C}_3\text{A}\Sigma_3\text{H}_{31}$  alone at room temperature (Figs. 1B and 1C). Over the same temperature range, but when the concentration of the  $\text{Ca}(\text{OH})_2$  in the *combined* solutions was lower, there was either no immediate precipitate, or else hydrated  $\text{Al}_2\text{O}_3$  formed (cf. 10, p. 721).

The implication in the experiments just described that there may be a change in the relative stabilities of the two sulphoaluminates as the temperature is increased will be considered later.

*Method of Conducting Experiments*

Following Graham *et al.* (8), calcium-45<sup>3</sup> was first introduced into the liquid. About 0.05 g of solid and exactly 50 cc of liquid were next sealed in cylindrical steel tubes of 110-cc capacity which were lined with gold or silver (cf. 8). In order that the reaction mixtures might be kept continuously agitated, the tubes were attached to a slowly revolving wheel.

After periods of reaction of several days, the tubes were opened and the liquid separated either by filtration through a "fine" sintered-glass filter or by centrifugation. Using 25 cc

<sup>3</sup>Obtained from Atomic Energy of Canada Limited, Chalk River, Ontario.

of liquid, calcium was determined as the oxalate, and sulphate as  $\text{BaSO}_4$ ; alternatively, the sum of a sulphate measurement plus a titration with  $\text{HCl}$  was used to estimate calcium. Four 1/2-cc portions of liquid were also pipetted onto aluminum dishes. The calcium was then precipitated with ammonium oxalate, acetone was added to disperse the precipitate, and, when the samples were dry, the  $\text{Ca}^{45}$  activity was measured with a simple end-window Geiger-Mueller tube. The relation between the activity and composition of the liquid determined whether a reaction had occurred and the mechanism of the reaction.

Unless otherwise specified, the reactions took place at a temperature of  $25 \pm 0.5^\circ \text{C}$ .

### THEORY

Define "external" exchange as exchange which occurs between a liquid and ions located in the *outer* layers of a solid, and which proceeds irrespective of crystallographic differences between the ions of the solid; define "internal" exchange as exchange occurring between a liquid and a crystallographically determined fraction of a solid (7). Then, according to reference 7, the mechanisms of solid-liquid reactions may be classified in at least two ways. When rapid, multidirectional *external* exchange occurs in either the reacting or product solid, with or without a component of internal exchange in addition, it is convenient to consider mechanisms based on whether the reaction proceeds at the surfaces of the solids or in the interior, and thence to distinguish "surface" and "internal" mechanisms and mixtures thereof. When the external exchange is either slow or non-existent in both solids, though without restriction to the *internal* exchange, the degree of mixing with the liquid of successively reacting portions of the reacting solid is more important, and one then recognizes the alternatives of complete mixing ("through-solution" mechanism) and no mixing ("direct" mechanism), as well as intermediate situations. General equations giving the relations between the activity and composition of the liquid for these mechanisms are developed in reference 7, and it is shown that when, as in the present work, the reacting solid is initially inactive and the extent of *all* rapid, multidirectional exchange is slight, these equations reduce to

$$[1] \text{ "surface" or "through-solution" mechanism} \quad \text{fractional activity} = (A/a)^{m_2/(m_2-m_1)},$$

$$[2] \text{ "internal" or "direct" mechanism, } m_1 < m_2 \quad \text{fractional activity} = (A/a),$$

where "fractional activity" refers to the activity of the liquid in units of fraction of the initial value,  $a$  is the amount of labeled species (i.e. calcium) initially present in the liquid,  $A$  is the variable amount of labeled species in the liquid at any time, and  $m_1$  and  $m_2$  are the numbers of moles of labeled species in the formulae of, respectively, the reacting and product solids. Mixed mechanisms would give intermediate activities.

An important property of the "surface" and "through-solution" mechanisms is that they alone cause the specific activity of the liquid to progress from its initial value to a point *beyond* the equilibrium value as the reaction goes to completion (cf. Figs. 2A and 2B of reference 7).

When pure exchange rather than a reaction occurs, then analogous to equations [1] and [2] one has

$$[3] \quad \text{fractional activity} = a/(a+nb/m),$$

where  $m$  is the number of moles of labeled species in the formula of the solid,  $n$  is the *apparent* portion of  $m$  which is exchangeable, and  $b$  is the amount of labeled species

present in the solid. Equation [3] with the substitution  $n = m$  describes radioactive equilibrium.

## RESULTS

*Reaction and Exchange of  $C_3AH_6$  with  $Ca(OH)_2$  Solutions*

Though it is reasonably well-established that  $C_3AH_6$  is a stable phase in the system C—A—H at room temperature, it is interesting to demonstrate this stability in an indirect manner by determining if a solid-liquid reaction occurs when inactive  $C_3AH_6$  is placed in contact with a solution of  $Ca(OH)_2$  labeled with  $Ca^{45}$ . Results are given in Table I. Some word is perhaps required about those experiments in which a finite time is

TABLE I  
Activity changes when inactive  $C_3AH_6$  is added to solutions of  $Ca(OH)_2$  labeled with  $Ca^{45}$

Calcium in solid, <i>b</i> (mole×10 <sup>4</sup> )	Calcium in initial solution, <i>a</i> (mole×10 <sup>4</sup> per 50 cc)*	Duration of experiment in days		Observed activity (fraction of initial value)	Activity to be expected at radioactive equilibrium (eq. [3])	Extent of exchange, <i>n</i> (moles calcium per mole C <sub>3</sub> AH <sub>6</sub> ) (eq. [3])
		( <i>a</i> ) Before labeling	( <i>b</i> ) After labeling			
5.47	3.57	0	8	.83	.40	.40
3.71	3.41	0	25	.91	.48	.27
4.67	3.41	0	81	.85	.42	.38
3.19	3.20	1	7	.93	.50	.23
3.27	3.20	5	7	.81	.49	.69
3.75	3.20	8	7	.83	.46	.52
4.03	3.20	55	7	.78	.44	.67
7.92	8.71	2.5	1/24†	.92	.52	.29
			15/24	.93	.52	.25
			1	.90	.52	.37
			4	.86	.52	.54
Mean = 0.42±0.1						

\*One mole  $\times 10^4$  per 50 cc corresponds to 0.112 g CaO per liter. The final calcium contents of the solutions, A, were very close to the initial calcium contents

†Four successive samplings were made in the final experiment.

indicated *before* labeling. In these experiments, in contrast to all others, the activity was added as concentrate to the centrifuged mixtures at the times indicated. "Initial" values for the activity were then derived by shaking the mixtures for 1 minute, centrifuging again, and sampling.

A decision as to whether  $C_3AH_6$  is stable is not possible simply on the basis of the observed lack of change in the composition of the liquid (Table I, footnote \*); thus, no change in composition would accompany such processes as solvation or crystal transformation. However, consider the activity changes. It was stated in Theory that the "surface" and "through-solution" mechanisms both cause the *specific* activity of the liquid to cross the equilibrium value as the reaction goes to completion. Noting that, in cases such as the present where the composition of the liquid remains essentially unchanged, *specific* activity is proportional to *total* activity, it is clear that such a relation is not observed (Table I, columns 5 and 6).  $C_3AH_6$  is therefore stable with respect to any reactions following the stated mechanisms. The significance of this is that, as will be shown in the Discussion, these mechanisms may be expected with high probability.

The observed activity changes can evidently be attributed to exchange. Since knowledge of the exchange behavior of  $C_3AH_6$  is required in the following section, values of the quantity  $n$  as defined by equation [3] have been included in Table I (final column). It



will be noted that a low, though rather fluctuant, limiting value of  $n$  was reached within an hour and that this value persisted even when the solid had been kept in contact with the liquid for up to two months prior to labeling. The exchange is thus slight in extent, rapid, and multidirectional. These are the characteristics, of course, of either surface exchange or multidirectional recrystallization, both of which will in general fall within the broader category of "external" exchange, as defined earlier.

*Reaction of  $C_3AH_6$  with Mixed  $Ca(OH)_2$ - $CaSO_4$  Solutions*

When  $C_3AH_6$  was added, not to a solution of  $Ca(OH)_2$  as in the preceding section, but to a mixed  $Ca(OH)_2$ - $CaSO_4$  solution, both the composition and activity of the solution changed markedly (see Table II). The changes in composition, as plotted in Fig. 2,

TABLE II  
Reaction of inactive  $C_3AH_6$  with mixed  $Ca(OH)_2$ - $CaSO_4$  solutions labeled with  $Ca^{45}$

Calcium in solid, $b$ (mole $\times 10^4$ )	Initial composition of solution (mole $\times 10^4$ per 50 cc)		Loss from solution (moles per mole $C_3AH_6$ )*			Calcium in final solution, $A$ (mole $\times 10^4$ per 50 cc)	Duration of experiment (days)	Observed activity (fraction of initial value)
	(a) Calcium, $a$	(b) Sulphate	(a) $Ca(OH)_2$	(b) $CaSO_4$	(c) Total $CaO$			
3.61	14.81	5.43	0	0.11	0.11	14.68	1/2	.99
"	"	"	0.13	0.40	0.53	14.16	1	.93
"	"	"	0	1.38	1.38	13.15	3	.77
"	"	"	0.27	2.60	2.87	11.35	6	.61
"	"	"	0.20	2.68	2.88	11.34	14	.62
3.97	14.36	5.22	0.21	1.47	1.68	12.13	3	—†
3.61	14.47	5.24	0	2.44	2.44	11.54	5	—
"	"	"	0.42	2.67	3.09	10.76	12	—
"	"	"	0.49	2.90	3.39	10.39	23	—
4.05	14.64	5.68	0.14	1.44	1.58	12.51	3	.75
4.07	"	"	0.20	2.78	2.98	10.59	7	.53
3.97	"	"	0.10	2.88	2.98	10.71	14	.55
4.04	8.17	7.08	0.06	0	0.06	8.09	3	.98
4.22	"	"	0.16	2.90	3.06	3.86	7	.25
3.86	"	"	0.20	2.89	3.09	4.19	14	.28
4.72	"	"	0.17	2.88	3.05	3.38	70	.19

\*To convert to mole  $\times 10^4$ , multiply by (calcium in solid)/3. Then (total  $CaO$ ) =  $a - A$ .

†No activity was present in the sixth to ninth experiments. In a further experiment similar to these, activity was added as concentrate on the 10th day. The total resulting exchange was as follows:  $n = 0.1, 0.6, 0.8$ , and  $0.9$  in, respectively, 1/24, 1, 5, and 12 days. The exchange is thus rapid relative to the rate of reaction, though may be only partially multidirectional.

indicate that the sulphoaluminate  $C_3A\bar{\Sigma}_3H_{31}$  has formed, the reaction time being about six days. The presence of this compound was confirmed by microscopic examination (Fig. 1B).

The interrelations between activity and composition enable the reaction mechanism to be determined. Note in this regard that the extent of *all* rapid, multidirectional exchange between the liquid and both solids was slight; thus for  $C_3AH_6$ ,  $n/m = 0.42/3$  (Table I), while for  $C_3A\bar{\Sigma}_3H_{31}$ ,  $n/m \leq 0.6/6$  (Table II, footnote †). Hence equations [1] and [2] are valid, with the former assuming the form  $(A/a)^2$  for  $m_1 = 3$ ,  $m_2 = 6$ . The theoretical activities according to equations [1] and [2], and the observed values as given in Table II, are compared in Fig. 3 (outer curves only). The indication is that the reaction follows a pure "surface" or "through-solution" mechanism, of which the former is more realistic since the exchange observed with  $C_3AH_6$  probably fell within the definition of "external".



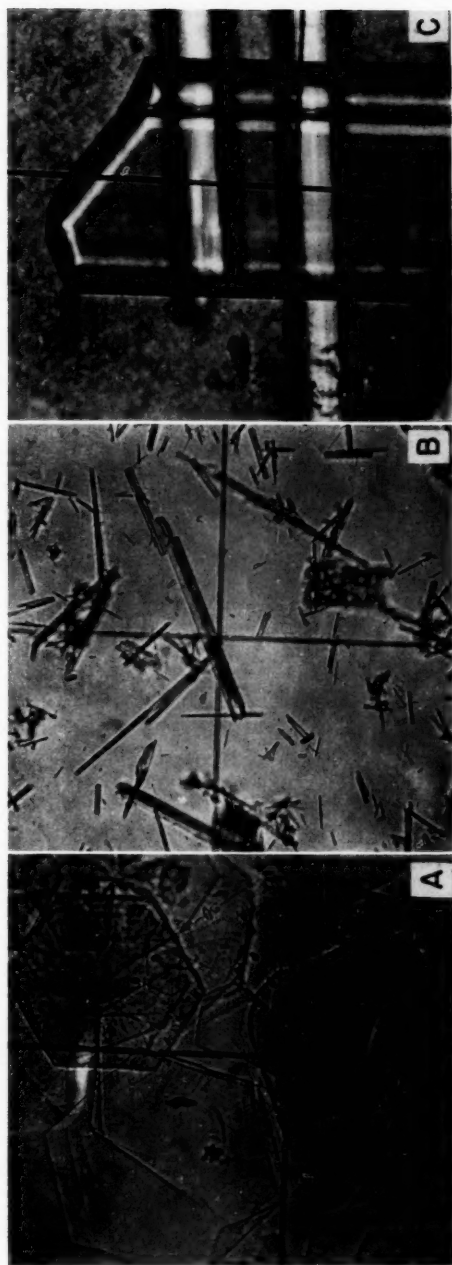
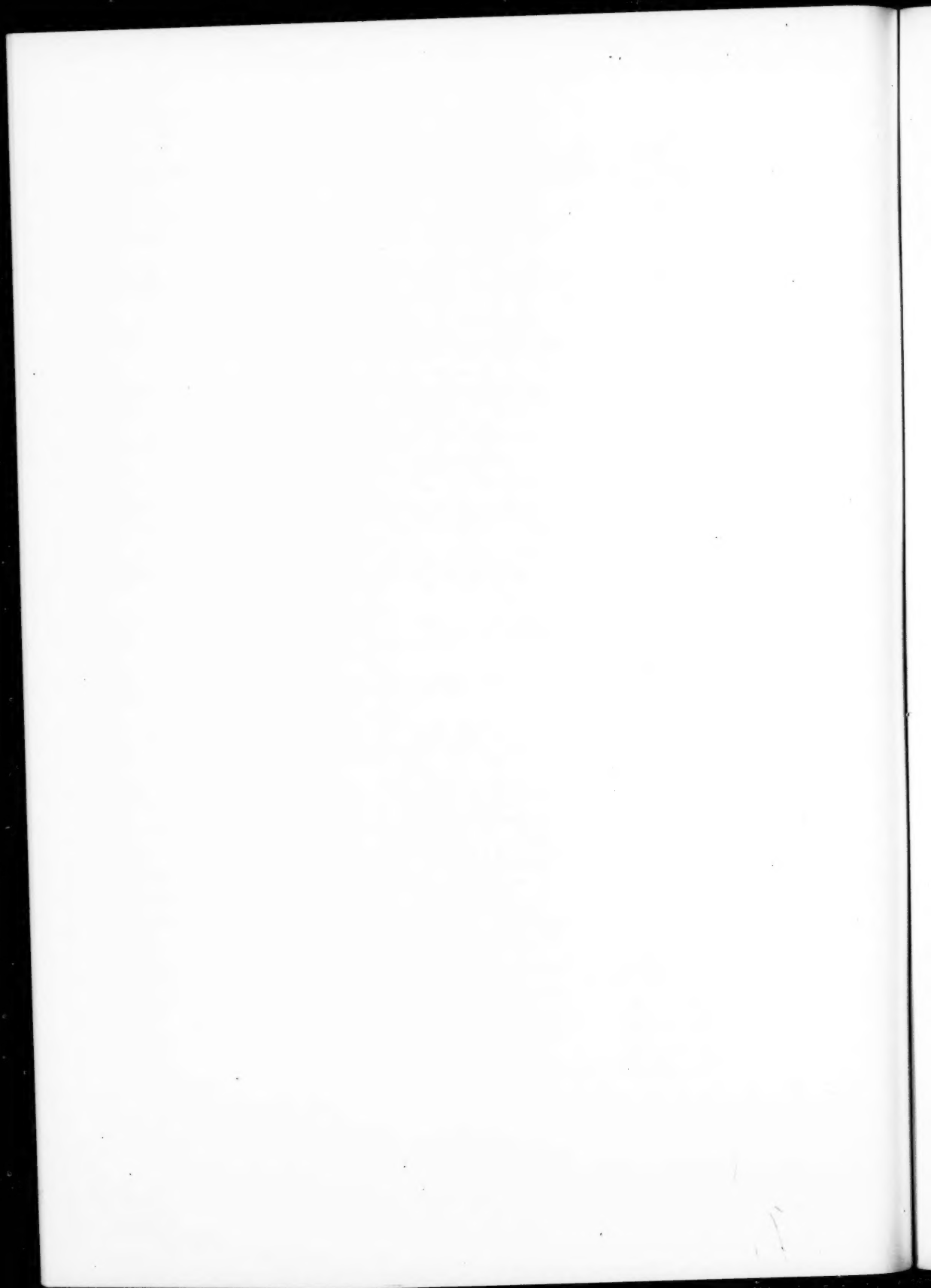


FIG. 1. Photomicrographs without nicols,  $\times 360$ . (A) Plates of  $C_3A_2H_{12}$  prepared by mixing *boiling* solutions of  $Al_2(SO_4)_3$ ,  $CaSO_4$ , and  $Ca(OH)_2$ . (B)  $C_3A_2H_{12}$  needles prepared by mixing *unheated* solutions of  $Al_2(SO_4)_3$ ,  $CaSO_4$ , and  $Ca(OH)_2$ . (C) Giant crystals of  $C_3A_2H_{12}$  obtained as before but with the mother liquor allowed to partially evaporate.



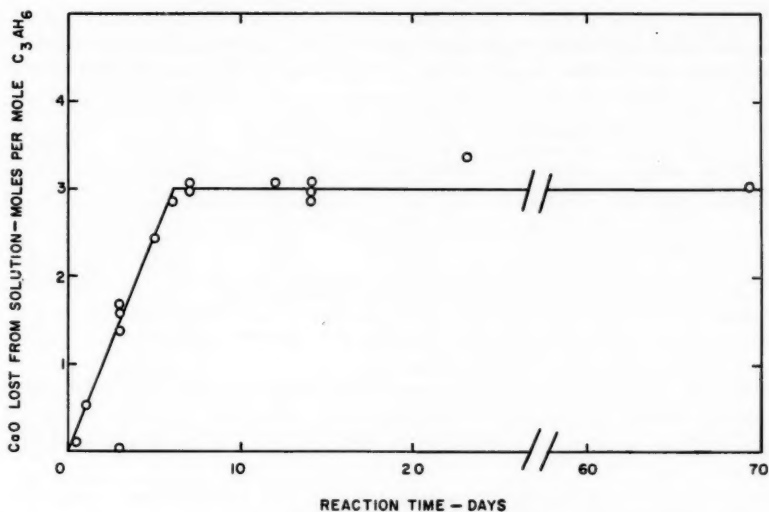


FIG. 2. Rate curve for the conversion of  $C_3AH_6$  to  $C_3A\Sigma_3H_{31}$  in mixed  $Ca(OH)_2$ - $CaSO_4$  solutions.

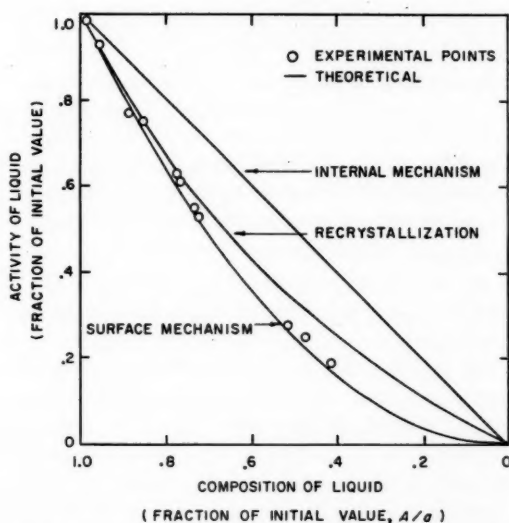


FIG. 3. Conversion of  $C_3AH_6$  to  $C_3A\Sigma_3H_{31}$  in mixed  $Ca(OH)_2$ - $CaSO_4$  solutions labeled with  $Ca^{48}$ : comparison of the observed activity of the liquid (in units of fraction of the initial value) with various predictions as functions of the composition of the liquid (again in units of fraction of the initial value, i.e.  $A/a$ ).

#### Reaction of $C_3A\Sigma H_{12}$ with Mixed $Ca(OH)_2$ - $CaSO_4$ Solutions

The reaction of  $C_3A\Sigma H_{12}$  with mixed  $Ca(OH)_2$ - $CaSO_4$  solutions is of general interest, since it not only demonstrates the relative stabilities of the two sulphoaluminates in the solutions used, but may be considered representative of the behavior of the entire solid-solution series  $C_3AH_{12}$ - $C_4A\Sigma H_{12}$ - $C_4AH_{12}$ . The results are given in Table III, from which

TABLE III  
Reaction of inactive  $C_3A\bar{\Sigma}H_{12}$  with mixed  $Ca(OH)_2$ - $CaSO_4$  solutions labeled with  $Ca^{45}$

Calcium in solid, $b$ (mole $\times 10^4$ )*	Loss from solution (moles calcium per mole $C_3A\bar{\Sigma}H_{12}$ )†	Duration of experiment (days)	Observed activity (fraction of initial value)	Predicted activities		
				(a) Surface or through-solution	(b) Internal or direct	(c) Re-crystallization‡
6.43	2.08	3	.45	.43	.76	.51
6.63	1.97	4	.42	.42	.75	.50
6.68	(Lost)	9	.46	.42	.75	.50
6.88	2.14	15	.42	.40	.74	.49

\*Samples of  $C_3A\bar{\Sigma}H_{12}$  having analyses near  $C_3A\bar{\Sigma}H_{10}$  (formula weight = 586.5) were used.

†The original solutions contained, per 50 cc,  $13.13 \times 10^{-4}$  mole calcium (a) and  $8.8 \times 10^{-4}$  mole sulphate.

‡Using the relation, fractional activity =  $(a-b/2)/(a+b)$ , as obtained from equation [13] of reference 7.

it can be seen that the loss of calcium from solution always corresponds to the complete conversion of the  $C_3A\bar{\Sigma}H_{12}$  to  $C_3A\bar{\Sigma}_3H_{31}$ . In agreement with this, the large flat hexagons of  $C_3A\bar{\Sigma}H_{12}$  (Fig. 1A) were always found to be replaced by fine needles (Fig. 1B), even in the 3-day experiment.

Again equations [1] and [2] may be used to correlate the activity and composition of the liquid for the various possible mechanisms. However, since the reaction was complete, it is convenient to replace the variable  $A$  with  $b$  (the amount of labeled species initially present in the reacting solid). Noting that  $b$  is given by  $A = a+b-m_2b/m_1$  (cf. equation [4] of reference 7), where  $m_1 = 4$  and  $m_2 = 6$ , the result is

"surface" or "through-solution" mechanism      fractional activity =  $(1-b/2a)^2$ ,

"internal" or "direct" mechanism                      fractional activity =  $(1-b/2a)$ .

The theoretical and observed activities are compared in Table III (columns 4 to 6). A pure "surface" or "through-solution" mechanism is indicated, though a decision between these mechanisms cannot be made from the limited exchange data available.

#### Reactions at Elevated Temperatures

It will be recalled that the method used for preparing  $C_3A\bar{\Sigma}H_{12}$  involved mixing boiling solutions of  $Al_2(SO_4)_3$ ,  $CaSO_4$ , and  $Ca(OH)_2$  (see Experimental). A final group of experiments was therefore undertaken to determine if  $C_3A\bar{\Sigma}H_{12}$  could also be obtained as a product of a solid-liquid reaction. Samples of  $C_3AH_6$  and  $C_3A\bar{\Sigma}H_{12}$  weighing about 0.05 g were added to 50-cc portions of a mixed  $Ca(OH)_2$ - $CaSO_4$  solution such that each portion contained  $13.32 \times 10^{-4}$  mole calcium and  $6.45 \times 10^{-4}$  mole sulphate, and were shaken inside an oven for periods of up to 7 days. For temperatures of 70° and 90° C the reaction products were consistently acicular, and solution analyses confirmed that  $C_3A\bar{\Sigma}_3H_{31}$  had formed.  $C_3A\bar{\Sigma}H_{12}$  can therefore *not* be obtained as a product of a solid-liquid reaction under the conditions of the experiments.

Though the solutions were labeled, the rapid attainment of radioactive equilibrium made it impossible to distinguish different reaction mechanisms.

#### DISCUSSION

##### Stabilities.

Little need be said about the observed stability of  $C_3AH_6$  in  $Ca(OH)_2$  solutions at 25° C. On the other hand, it is significant that at 25°, 70°, and 90° C the compounds  $C_3AH_6$  and  $C_3A\bar{\Sigma}H_{12}$  consistently reacted with mixed  $Ca(OH)_2$ - $CaSO_4$  solutions to form

$C_3A\Sigma_3H_{31}$ .  $C_3A\Sigma_3H_{31}$  thus appears to be the stabler sulphoaluminate over the entire temperature range  $25^\circ$  to  $90^\circ$  C, so that the ready formation of  $C_3A\Sigma H_{12}$  by mixing hot solutions, as described earlier, must have been associated with a greater *crystallizability*, as distinct from *stability*, for this compound at elevated temperatures.

### Mechanisms

From the observed relations between the activity and composition of the liquid, the  $C_3AH_6$ - $C_3A\Sigma_3H_{31}$  reaction was concluded to proceed with a "surface" mechanism, and the  $C_3A\Sigma H_{12}$ - $C_3A\Sigma_3H_{31}$  reaction with either a "surface" or "through-solution" mechanism. Now, in making the various calculations to determine mechanisms, the extent of *all* rapid, multidirectional exchange between the liquid and both solids was assumed to be slight; or, what is equivalent,  $n_1$  and  $n_2$  (the portions of  $m_1$  and  $m_2$  undergoing rapid, multidirectional exchange, whether external or internal) were approximated as approaching zero. It is interesting to consider what the activity predictions would have been for the  $C_3AH_6$ - $C_3A\Sigma_3H_{31}$  reaction had the actual values of  $n_1$  and  $n_2$  been taken into account. Introducing  $n_1 = 0.42$  (Table I) and  $n_2 \sim 0.6$  (Table II, footnote †) into equation [1] of reference 7, substituting the latter into equation [3] of reference 7, and assuming the reaction to be complete, one obtains

$$[4] \quad \text{fractional activity} = \frac{1-b/a}{1+0.42b/3a} \left\{ 1 - \frac{2.82b}{3a+0.42b} \right\}^{0.915}.$$

For the case  $a = 4b$  (as in the first experiments of Table II), equation [4] yields 0.572, to be compared with 0.563 from equation [1]. Similarly for  $a = 2b$  (as in the last experiments of Table II) one obtains, respectively, 0.276 and 0.250 from the full and abbreviated expressions. The differences in the activity predictions are thus not great, though the predictions using equation [4] lie in such a direction as to bring about a slightly better fit between experiment and theory (cf. Fig. 3).

A more serious difficulty than the presence of various *known* exchange processes in determining solid-liquid reaction mechanisms is the possibility that the freshly formed product solid may have been subject to unexpectedly extensive recrystallization, or else that long-lived (i.e. non-transient) solid intermediates may have occurred. As pointed out in reference 7, these effects tend to make the activity the same for all mechanisms in the later stages of reaction. Thus for the  $C_3AH_6$ - $C_3A\Sigma_3H_{31}$  reaction, assuming  $n_1 \rightarrow 0$ , the activity would always be close to (from equation [13] of reference 7)

$$[5] \quad \text{fractional activity} = \frac{A/a}{2-A/a}.$$

Equation [5] is plotted in Fig. 3, where it is seen that, while the experimental data for high values of  $A/a$  are equally consistent with either equations [1] or [5] and therefore quite ambiguous (cf. 8, p. 141-142), the three experiments with low  $A/a$  still point to a simple "surface" mechanism. The originally proposed mechanisms also appear to be adequate for the  $C_3A\Sigma H_{12}$ - $C_3A\Sigma_3H_{31}$  reaction (see Table III, columns 4, 5, and 7).

No substantial objection to assigning "surface" or "through-solution" mechanisms to the reactions studied appears to exist. Four other reactions have also been shown to follow one or the other of these mechanisms:<sup>4</sup> the hydrations of  $3CaO \cdot SiO_2$ ,  $2CaO \cdot SiO_2$

<sup>4</sup>In the original work these reactions are all described as following a "through-solution" mechanism. However, as pointed out in reference 7, there is reason to believe that the hydrations of  $CaSO_4 \cdot \frac{1}{2}H_2O$  and dead-burnt  $CaO$ , in particular, are actually more nearly consistent with a "surface" mechanism.

(8),  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  (12), and dead-burnt  $\text{CaO}$  (13). In only one case has a different mechanism been observed: the hydration of soft-burnt (i.e. porous)  $\text{CaO}$  (13), which proceeds with a mixture of "surface" and "internal" mechanisms (cf. footnote 4). It therefore seems likely that, except with porous substances, a "surface" or "through-solution" mechanism occurs *invariably*. Which of these two mechanisms will prevail in individual cases depends, of course, on the presence or absence of rapid, multidirectional *external* exchange; however, *surface* exchange is probably always multidirectional and external, and is usually also rapid (14), so that the "surface" mechanism may be expected to be generally applicable.

#### ACKNOWLEDGMENTS

The work described here was carried out under the direction of Dr. T. Thorvaldson of this department. Dr. Thorvaldson's assistance is gratefully acknowledged.

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## NOTES

### A NOTE ON THE CYCLIZATION OF 3-(2'-NAPHTHYL)-BUTYRIC ACID

P. M. G. BAVIN

In reporting the ultraviolet spectra of some polyalkylphenanthrenes prepared by Haworth and his co-workers, Askew (1) noted that three of them showed additional peaks at wavelengths longer than those expected for phenanthrene derivatives. The anomalous peaks are collected in Table I for comparison with the longest wavelength

TABLE I

	Anomalous peaks (m $\mu$ )		
1,7-Dimethylphenanthrene	381	371	359
2,3-Dimethylphenanthrene	379		358
1,6,7-Trimethylphenanthrene	380		360
Anthracene (5, p. 175)	374.5		354.5

peaks of anthracene. There can be little doubt that the polyalkylphenanthrenes contained at least traces of the corresponding alkylanthracenes since the observed spectral shifts are of the order expected for two or three methyl substituents, if it is assumed that the shifts are additive. This assumption is widely accepted (2) and is supported by published spectra of polyalkylphenanthrenes (1, 3) and polyalkylnaphthalenes (2). (For the spectrum of 9-methylanthracene see ref. 4 and ref. 5 (p. 63) and for the spectrum of 1-methylanthracene see ref. 6. The spectrum of 2-methylanthracene has not been published but the effect of the methyl group has been obtained by difference (2).)

The cyclization of 3-(2'-naphthyl)-butyric acid by hydrogen fluoride has now been examined. The crude neutral product was successively reduced and dehydrogenated to give phenanthrene containing 2% anthracene, as determined spectroscopically.

These results emphasize the difficulty of obtaining pure compounds by routes involving cyclization, and show that, like most substitution reactions of naphthalene, both  $\alpha$  and  $\beta$  products are to be expected. Cyclizations occurring predominantly at a  $\beta$ -position may be attributed to steric hindrance (7, 8, and references therein).

1-Aza-anthracene could not be detected among the products of the Skraup reaction on 2-aminonaphthalene, possibly because of the ease with which it is oxidized (9).

### EXPERIMENTAL

Pure 3-(2'-naphthyl)-butyric acid (2.7 g), prepared from naphthalene, was dissolved in hydrogen fluoride (150 ml) and the solution left at room temperature for 48 hours. The neutral product was reduced (Clemmensen-Martin) and the crude hydrocarbon dehydrogenated (10% palladium on charcoal at 300°). The crude aromatic hydrocarbons dissolved in hexane were passed through a short (1×1 in.) column of activated alumina to remove traces of tar, elution being continued with benzene-hexane (1:5) to recover all the product. The eluted material was dissolved in ethanol and the ultraviolet spectrum recorded, using a Beckmann DK-2 recording spectrophotometer. Comparison with

standard mixtures\* showed the phenanthrene to contain 2% anthracene. For the analysis, anthracene peaks at 376 and 357 m $\mu$  (cf. 5, p. 175) and phenanthrene peaks at 339, 330, and 323 m $\mu$  (cf. 5, p. 142) were used.

A separate experiment established that phenanthrene was not isomerized on the palladium catalyst.

The products from the Skraup reaction on 2-aminonaphthalene (11) were dissolved in hot heptane and passed through a column of alumina to remove tar, elution being continued with benzene-hexane (1:5) to recover all of the products. The eluted material was fractionally crystallized from ethanol to show that at least 95% was 1-aza-phenanthrene. The residues were chromatographed (hexane-alumina) and the ultraviolet spectra recorded for successive fractions. Those fractions showing peaks at wavelengths longer than 360 m $\mu$  were examined further,† by descending chromatography on buffered paper (12) at pH's 3 and 6, using *n*-butanol saturated with water as solvent. Spots located under an ultraviolet lamp were eluted with ethanol and the spectra of the solutions recorded. A trace of an unidentified compound was detected, having characteristic absorption peaks at 396, 386, and 375 m $\mu$ . (1-Aza-anthracene has peaks at 384, 366.5, 356.5, and 340 m $\mu$  (13) and these values were confirmed by preparing and examining an authentic specimen (14).)

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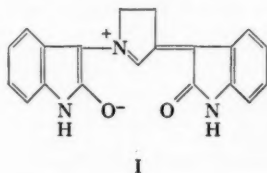
\*Pure and puriss grades of phenanthrene from several sources contained 1-2% anthracene, removed by reaction with maleic anhydride (10).

†The author is indebted to Dr. C. R. Eves, R.C.M.P., for these experiments.

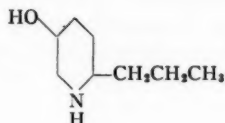
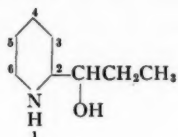
## A COLOR TEST FOR CERTAIN PIPERIDINE AND PYRROLIDINE ALKALOIDS\*

D. J. McCALDIN†

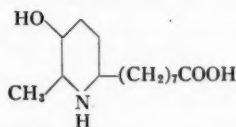
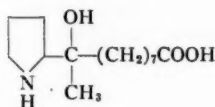
The blue color formed from isatin and proline has frequently been used as a method for detecting this imino acid after paper chromatography (1). On the basis of recent work (2) the structure of this pigment has been revised (I), and it is now possible to extend the use of the reaction for the detection of similar compounds in alkaloidal extracts.



The test described is specific for alkaloids with a single six- (or five-) membered ring containing the sequence  $\text{—NH—CH}_2\text{—CH}_2\text{—}$ . Thus conhydrine (II) gives a positive reaction whereas  $\psi$ -conhydrine (III) does not, owing to the presence of substituents in both the 2 and the 5 positions.



Previous workers (3) suggested that the sequence required for pigment formation was  $\text{—CH}_2\text{—NH—CH}_2\text{—}$ , and the earlier structure proposed for carpamic acid (IV) was based on its negative reaction with isatin (4). In fact, a compound with this structure would be expected to react, whereas the revised structure (V) would not (5).



Certain  $\alpha$ -imino acids, such as 4-hydroxyproline, do not appear to contain the arrangement of atoms necessary for color development. However, the carboxyl group is lost in each case during the reaction and the conditions for pigment formation are thus fulfilled. The negative results obtained from hygrine, stachydrine, hygric acid, and N-methylpipecolic acid can be explained by the absence of the  $\text{—NH—}$  group. Azetidine 2-carboxylic acid (6) and hexamethyleneimine did not react normally, showing that ring

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†National Research Council Postdoctorate Fellow.

size is a critical factor. An imino acid extracted from apples (11) also yields a positive result in this test, and is tentatively regarded as 4-hydroxymethylproline.

This method of detecting certain alkaloids after paper chromatography can be used in conjunction with other techniques. The individual components of a mixture of such compounds may be detected in the following manner. The chromatogram is sprayed

TABLE I  
Color obtained with isatin reagent

Alkaloid	Color	Alkaloid	Color
Azetidine 2-carboxylic acid	—	4-Hydroxypipelicolic acid (9)	Brown
Proline	Blue	5-Hydroxypipelicolic acid (10)	Blue
4-Hydroxyproline	Blue	Piperazine	Blue
3-Methylproline	Blue	Conhydrine	Blue-green
4-Methylproline (7)	Blue	$\psi$ -Conhydrine	—
norHygrine (8)	Blue	Coniine	Blue
Stachydrine	—	isoPelletierine (8)	Blue
3-Hydroxypipelicolic acid (9)	Blue	Anabesine	—
		Hexamethyleneimine	—

with isatin, baked, and subsequently treated with Dragendorff's reagent (12). Hygric acid and N-methylpipelicolic acid are shown to be present when the paper is first treated with potassium permanganate (to remove the N-methyl group). Other N-methylated compounds, such as methyl hygrate, are not converted to the corresponding secondary imines.

#### EXPERIMENTAL

##### General Method

A descending one-dimensional paper chromatographic technique was used to separate and detect a typical mixture of proline and coniine. The mixture and reference compounds were placed on a paper strip (Whatman No. 1) and developed with the upper phase of a butan-1-ol-acetic acid-water (4:1:5 by volume) mixture as solvent. The detecting agent was a 0.1% (w/v) solution of isatin in aqueous acetic acid (5%). Since coniine is rather volatile, the developed chromatogram was only partially dried (15 minutes at room temperature) before it was sprayed with the isatin solution. The colors developed after baking in the oven at 130° for 5 minutes; the proline spot had  $R_F = 0.39$ , and the coniine spot  $R_F = 0.81$  at 25°.

##### Detection of Hygric Acid or N-Methylpipelicolic Acid

Two paper strips were prepared and developed as described above. The chromatograms were dried and a cold, saturated solution of potassium permanganate in a mixture of acetone and pyridine (95:5) was sprayed onto one paper. The positions of the chromatographed materials were apparent from the appearance of yellow spots on the purple background. The corresponding areas on the second chromatogram were then sprayed with the oxidant and the paper dried at room temperature. It was then treated in the normal manner as previously described.

#### ACKNOWLEDGMENTS

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




### SOME NEW BENZILIC ACID DERIVATIVES

FRANCIS L. CHUBB, GERASSIMOS FRANGATOS, AND JACQUELINE NISSENBAUM

Morrison, Konigstein, and Cohen (1) have synthesized a series of esters of benzilic acid (I) related in structure to benadryl and trasentin. Klosa (2) has also reported that 2-dimethylaminoethyl esters of alkoxydiphenylacetic acid (II) possess strong analgesic and sedative action. In this communication we wish to describe the synthesis of some new benzilic acid derivatives similar in structure to both I and II. These compounds (III-VI) are listed in Table I. The intermediates required for their preparation are listed in Table II.

TABLE I  

$$\begin{array}{c} \text{O}-\text{CH}_2\text{CH}_2\text{R} \\ | \\ (\text{C}_6\text{H}_5)_2\text{C}-\text{COOCH}_2\text{CH}_2\text{R}_1 \end{array}$$

Compound	R	R <sub>1</sub>	Yield, %	M.p. or b.p.	Formula	Analysis*					
						Calculated			Found		
						C	H	N	C	H	N
III	Cl	 .HCl	51	145-148°	C <sub>20</sub> H <sub>18</sub> NO <sub>2</sub> Cl <sub>2</sub>	60.32	6.33	3.52	61.3	6.61	3.72
IV	H	 .HCl	64	166-168°	C <sub>21</sub> H <sub>18</sub> NO <sub>2</sub> Cl	67.76	7.21	3.59	67.72	7.24	3.59
V	H	 O.HCl	80	172-174°	C <sub>22</sub> H <sub>18</sub> NO <sub>3</sub> Cl	65.08	6.95	3.45	64.82	7.06	3.45
VI			74	195-197/1 mm	C <sub>26</sub> H <sub>18</sub> N <sub>2</sub> O <sub>2</sub>	73.55	8.55	6.60	73.11	8.44	6.75

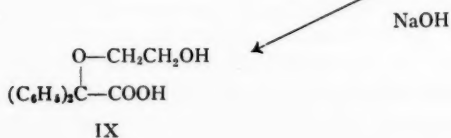
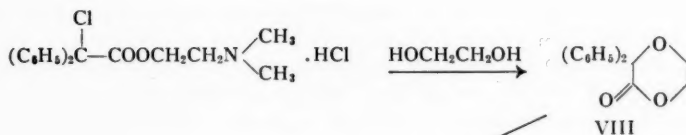
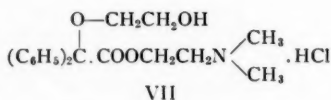
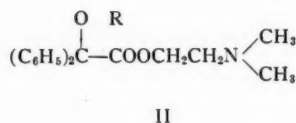
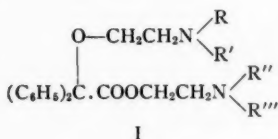
\*Calc.: for III Cl, 17.80. Found: Cl, 17.92.

When an attempt was made to prepare dimethylaminoethyl diphenyl(2-hydroxyethoxy) acetate hydrochloride (VII) by the reaction of ethylene glycol with dimethylaminoethyl chlorodiphenylacetate hydrochloride, ring closure to form the cyclic lactone VIII occurred. Alkaline hydrolysis converted VIII to the corresponding acid IX.

TABLE II  
Intermediates  $(C_6H_5)_2\overset{\overset{R}{|}}{C}-COOR'$

R	R'	M.p. or b.p.	Yield, %	Formula	Analysis					
					Calculated			Found		
					C	H	N	C	H	N
OH	$CH_2CH_2N\begin{smallmatrix} CH_3 \\   \\ CH_3 \end{smallmatrix}$ HCl	150-160 <sup>aa</sup>	57							
OH	$CH_2CH_2N\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ .HCl	174-175 <sup>ab</sup>	78							
OH	$CH_2CH_2N\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ O.HCl	178-180 <sup>ac</sup>	61							
Cl	$CH_2CH_2N\begin{smallmatrix} CH_3 \\   \\ CH_3 \end{smallmatrix}$ .HCl	184-186 <sup>ad</sup>	83							
Cl	$CH_2CH_2N\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ .HCl	165-167 <sup>e</sup>	88	$C_{29}H_{21}NO_2Cl$	63.17	6.10	3.68	63.13	6.12	3.75
Cl	$CH_2CH_2N\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$ O.HCl	139-140 <sup>ae</sup>	81							
$OCH_2CH_2N\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$	$C_2H_5$	195-197°/1 mm	58	$C_{22}H_{19}NO_2$	74.54	7.96	3.95	74.74	7.72	4.34
$OCH_2CH_2N\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix}$	Na	291-292°	81	$C_{28}H_{21}NO_2Na$	68.95	6.65	4.02	69.24	6.51	4.13

<sup>a</sup>Lit. value 184-186° (5). <sup>b</sup>Lit. value 173-173.5° (6). <sup>c</sup>Lit. value 181.5-182.5° (6). <sup>d</sup>Lit. value 183-185° (4). <sup>e</sup>Lit. value 151.5-152° (7).





## EXPERIMENTAL

*Dialkylaminoethyl Benzilate Hydrochlorides* (Table II)

These compounds were prepared from benzoic acid and the required 2-chloroethyl-dialkylamine according to the general method of Horenstein and Pahllicke (3).

*Dialkylaminoethyl Alkoxydiphenylacetate Hydrochlorides* (Table I)

Compounds III, IV, and V were prepared from the dialkylaminoethyl benzilate hydrochlorides by way of the corresponding chlorodiphenylacetate hydrochlorides as described by Klosa (4). Details of the preparation of dimethylaminoethyl 2-chloroethoxydiphenylacetate (III) are given below, since Klosa's procedure was modified in this case.

A mixture of 15 g of dimethylaminoethyl chlorodiphenylacetate hydrochloride, 3 g of calcium carbonate, and 76 ml of freshly distilled 2-chloroethanol was refluxed for 24 hours with mechanical stirring. The hot reaction mixture was filtered and then allowed to cool. The solvent was distilled under reduced pressure and the residue extracted with acetone and filtered. After distillation of the acetone the residue was treated with 200 ml of 10% sodium hydroxide and extracted with ether. The dried ether layer (calcium chloride) was then saturated with hydrogen chloride at 3 to 4°. The hydrochloride precipitated as a crystalline product, 8.5 g (51%), m.p. 145–151°.

The material was purified by dissolving it in isoamyl alcohol and slowly pouring the resulting solution into anhydrous ether containing some seed crystals, m.p. 145–148°. The mixture was not stirred but kept overnight at 5°. Filtration yielded crystals melting at 145–148°.

*Diethylaminoethyl 2-(1-Pyrrolidyl)ethoxydiphenylacetate* (VI)

This compound was prepared from ethyl benzilate according to the method of Morrison, Königstein, and Cohen (1).

*2,2-Diphenyl-3-keto-1,4-dioxane* (VIII)

A mixture of 20 g of dimethylaminoethyl chlorodiphenylacetate hydrochloride, 4.5 g of calcium carbonate, and 100 ml of ethylene glycol was heated for 24 hours at 90–100°. After the solution was filtered it was made basic with sodium hydroxide. The resulting solid was filtered and washed with dilute hydrochloric acid. After recrystallization from alcohol–water a yield of 8.5 g (59%), m.p. 95–97°, was obtained. A second recrystallization raised the melting point to 98–99°. Anal. Calc. for  $C_{16}H_{14}O_3$ : C, 75.59; H, 5.51. Found: C, 75.11; H, 5.62.

*Diphenyl(2-hydroxyethoxy)acetic Acid* (IX)

2,2-Diphenyl-3-keto-1,4-dioxane (1 g) was refluxed with 10 ml 10% sodium hydroxide for 2 hours. After dilution and acidification of the solution, the product, m.p. 122–123°, after recrystallization from alcohol–water, was obtained. Anal. Calc. for  $C_{16}H_{16}O_4$ : C, 70.6; H, 5.88. Found: C, 70.64; H, 6.06. Neut. eq. Calc.: 272. Found: 272.

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EFFECT OF NITRIC OXIDE IN THE  $\gamma$ -RADIOLYSIS OF ETHANE AT VERY LOW CONVERSIONS

KANG YANG

Back and Miller (1) investigated the radiolysis of gaseous saturated hydrocarbons at very low conversions. They found an important fact: The  $G(\text{H}_2)$  values corresponding to initial rates are approximately twice the values estimated at the higher conversions.

We investigated the formation of hydrogen in ethane and ethane - nitric oxide systems. Our results very closely agree with the results of Back and Miller and also with inhibition data of Back (2) using ethylene as a radical scavenger.

In this note we summarize our results. This probably strengthens the contribution of Back and Miller. In addition a new conclusion is drawn: nitric oxide scavenges hydrogen atoms with negligible effect on the nonradical processes leading to the molecular hydrogen in the ethane radiolysis.

## EXPERIMENTAL

Phillips' research grade ethane is carefully degassed by repeated evacuations at liquid nitrogen temperature and then subjected to four-stage bulb-to-bulb distillation each time retaining only the middle third. Purified ethane is introduced in Pyrex vessels (156 cc). The gamma source was four spent fuel elements from the Engineering Test Reactor, Arco, Idaho. Energy input rate was  $7.9 \times 10^{-4}$  electron volts per hour per molecule of ethane. This was estimated assuming that  $G(\text{H}_2)$  in methane radiolysis is 5.7 molecules per 100 electron volts (3).

Hydrogen in irradiated samples was analyzed by gas adsorption chromatography (silica gel column, argon carrier, room temperature).

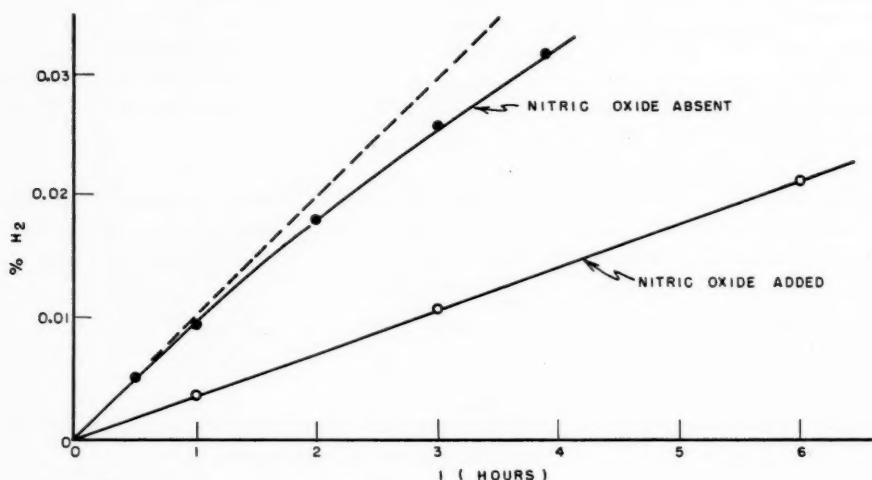


FIG. 1. Formation of hydrogen in ethane radiolysis in the presence and absence of nitric oxide.

## RESULTS AND DISCUSSION

In Fig. 1 the rate of formation of hydrogen is shown as a function of irradiation time. In the absence of nitric oxide, the rate decreases with increasing conversion. Initial rate estimated from Fig. 1 is 1.93 times the rate at 0.68% conversion of ethane.

In the presence of nitric oxide, the rate is constant. Estimated percentage of radical contribution to the hydrogen formation at the initial period of the reaction was 64% (4).<sup>\*</sup> The value is in close agreement with Back's result of 63% obtained using ethylene as a scavenger (2).

We have seen that both ethylene and nitric oxide give the same yield for the molecular hydrogen. This can best be explained by assuming that high enough concentrations of nitric oxide and ethylene to scavenge most of the hydrogen atoms had no measurable effect on the nonradical processes yielding molecular hydrogen, an important condition that a satisfactory radical scavenger in the radiolysis reactions should satisfy.

From Fig. 1 it is also clear that only  $G(H_2)$  due to radical reactions decreases with increasing conversion. This supports Back's explanation that decrease in  $G(H_2)$  at high conversion is due to the formation of unsaturated radiolysis products.

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<sup>\*</sup>This is much higher than the values estimated at the higher conversion.

## A MECHANISM FOR THE INDUCTIVE EFFECT

HENRY A. BENT

To the author's knowledge, no detailed mechanism has yet been given to explain the *modus operandi* of the inductive effect. It is the purpose of this note to propose a mechanism for the inductive effect and to show that this effect must be coupled in a predictable manner to certain differential changes in molecular geometry. The language chosen for the present discussion is the familiar language of valence-bond theory and hybrid atomic orbitals; although it may be noted that well-known, but for present purposes less convenient, alternatives do exist (1-5).

Discussion of the experimental evidence that has been marshalled in support of the present argument may be separated into two related parts: (1) the effect of electronegative groups on atom hybridization and (2) the effect of atom hybridization on electronegativity.

(1) *The Effect of Electronegative Groups on Atom Hybridization*

The XOY bond angles in  $CH_3OCH_3$ ,  $CH_3OH$ , and  $FOF$  are, respectively,  $111^\circ$  (6),  $109^\circ$  (7),  $105^\circ$  (8), and  $101^\circ 30'$  (5). In  $CH_3SH$  and  $HSH$  the bond angles are, respectively,  $100^\circ$  (9) and  $92^\circ$  (5). The same consistent decreases in interbond angle

with increasing electronegativity of the substituent group occurs in phosphorus and arsenic compounds (10) and in the series  $N(CH_3)_3$ ,  $NH_3$ , and  $NF_3$ , where the XNX interbond angles are, respectively,  $109^\circ$  (10),  $106^\circ 46'$  (10), and  $102^\circ 30'$  (5). Additional examples are cited by Mellish and Linnett (5). As noted by these authors, it is an interesting fact that changes in interbond angles are often in the reverse direction from what one would expect if repulsions between nonbonded atoms were the most important effect operating. In every case, it would appear that replacement of an atom or group of atoms by a group of greater electronegativity causes the atom on which substitution occurred to rehybridize in such a manner that some of its  $s$ -character is withdrawn from the orbital where substitution occurred. Further evidence of this may be obtained from a study of interatomic distances.

Currently there is increasing recognition of the suggestion that atom hybridization has an appreciable effect not only on bond angles, as is well known, but on bond lengths as well. Data bearing on this issue has been summarized recently by Brown (11). If the view that atom hybridization may have a pronounced effect on bond lengths is adopted, the conclusion is quickly reached that bond lengths decrease noticeably as the  $s$ -character in the bond increases. Typically, the carbon-carbon single-bond distance appears to decrease by about  $0.04 \text{ \AA}$  each time one of the participating carbon atoms changes hybridization from  $sp^3$  to  $sp^2$  or from  $sp^2$  to  $sp$ . For carbon-halogen bonds, the effect appears to be even more pronounced. While it is not our purpose here to offer a detailed explanation of these effects in terms of an hybridization-ratio-dependent covalent radius, we may note that preliminary considerations do suggest that such an explanation may be possible. Adoption of this hypothesis conjointly with the data on bond angles cited above leads to the supposition that bond lengths should vary with the electronegativity of adjacent substituents. Indeed, the noticeable foreshortening of bond lengths that occurs when fluorine atoms are introduced into molecules has been commented upon (12). For example, the C-F distance is  $1.391 \text{ \AA}$  in  $CH_3F$ , whereas it is only  $1.323 \text{ \AA}$  in  $CF_4$ . Numerous other examples exist in the current literature that illustrate the foreshortening that occurs in bond lengths when an atom of relatively low electronegativity, such as hydrogen, is replaced by an atom of greater electronegativity, such as fluorine, or one of the other halogens. It is interesting to note that the change in molecular parameters is again often in the reverse direction from what one would expect if repulsions between nonbonded atoms were the important effect operating.

If unshared pairs are regarded as electrons in a bond to an atom of zero electronegativity, the evidence cited above concerning the effect of electronegative groups on molecular geometry may be summarized in the statement: *The  $s$ -character of an atom tends to concentrate in orbitals that are directed toward electropositive groups.*

## (2) The Effect of Atom Hybridization on Electronegativity

Inductive constants for a carbon atom in an  $sp^3$  valency,  $sp^2$  valency, and an  $sp$

valency have been given by Taft (13). He finds  $H_3C- = -0.100$ ,  $CH_3C(=O)- = +0.60$ , and  $NC- = +1.300$ . On this scale the inductive constant for chlorine is  $+1.10$ . More recently, Petro has calculated from dipole moment data and infrared dispersion data these carbon-carbon bond moments:  $(sp^3)^+ - (sp^2)^- = 0.68D$ ,  $(sp^2)^+ - (sp)^- = 1.15D$ , and  $(sp^3)^+ - (sp)^- = 1.48D$  (14). He finds, also, that chlorine constitutes the positive end

of the C—Cl bond moment in  $\text{HC}\equiv\text{CCl}$ . These results provide strong confirmation of the statement by Mulliken (15) and Walsh (16) that *the more s-character in an atomic valency, the more electronegative is the atom in that valency*.

Combining these two attributes of the s-character of an atom, one obtains the following picture of the inductive effect. Consider the array A—X—B, and suppose that the electronegativity of the group at B increases. This change will cause X to rehybridize slightly, so as to shift some of its s-character from the bond B to the bond to A, where the low potential energy space characteristic of an s-orbital will be used to greater advantage. In effect, the electronegativity of X toward A becomes greater. In turn, by an identical, but smaller, operation of the same mechanism, the electronegativity of A toward attached groups (other than X) becomes greater.

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#### THIAZOLES. IV. PROTON MAGNETIC RESONANCE SPECTRA OF THIAZOLE AND ITS METHYL DERIVATIVES\*†

A. TAURINS AND W. G. SCHNEIDER

The proton resonance spectra of five-membered cyclic unsaturated compounds are of considerable interest not only from the standpoint of structure determination in complex organic molecules, but also in connection with the rather unusual proton spin-coupling interactions in these systems (1, 2, 3). In this connection the high-resolution proton resonance measurements of thiazole, which contains two heteroatoms in the five-membered ring, are of some interest. Figure 1 shows a reproduction of the proton

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†Thiazoles. III. A. Taurins, J. G. E. Fenyes, and R. N. Jones. *Can. J. Chem.* **35**, 423 (1957).

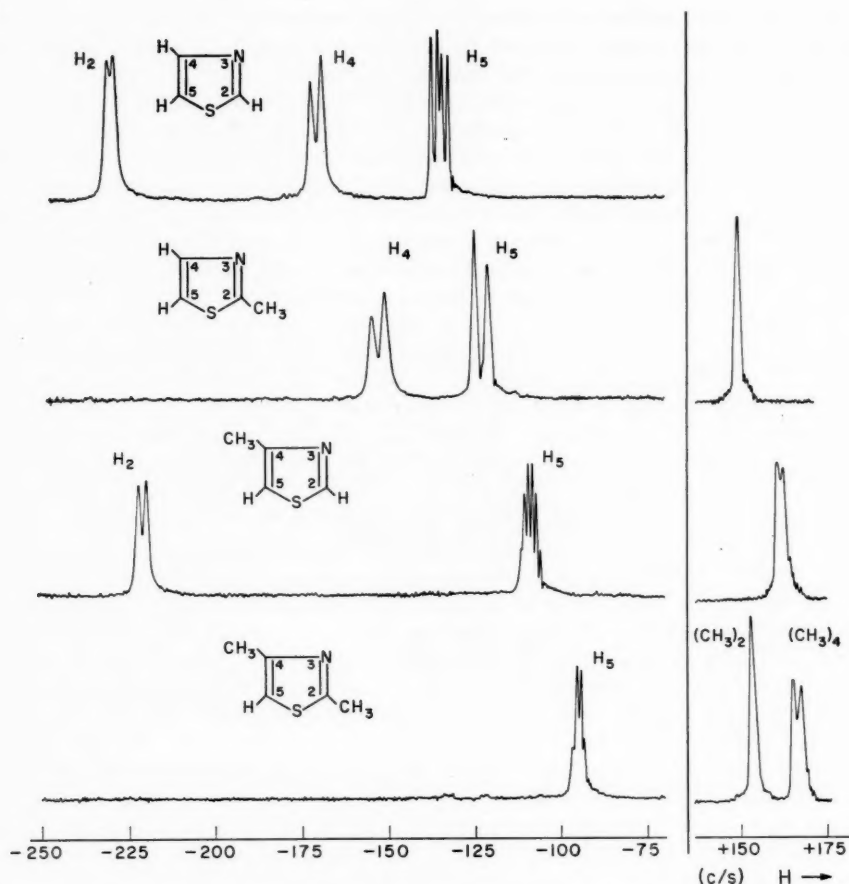


FIG. 1. Proton magnetic resonance spectra of thiazole and its methyl derivatives at 60 Mc/s. Samples were measured as the pure liquids. Frequency scale is relative to an external water reference. The signals of the methyl group protons were recorded at a lower gain than those of the protons bonded to the thiazole ring.

resonance spectrum at 60 Mc/s for thiazole and for three methyl derivatives. With the aid of the spectra of the latter compounds an unambiguous assignment can be made for the parent compound, as shown in Fig. 1. The measured chemical shifts and spin-coupling constants for the protons bonded to the ring are summarized in Table I. The additional signals arising from the methyl substituents, which appear on the high field side of the reference water signal, are also shown in Fig. 1. A splitting of about 1 cycle/second between proton 5 and a methyl group in the 4 position is observed.

The most striking features of the above spectra are the relatively broad signals arising from the protons at positions 2 and 4, and in contrast, the sharp signal arising from the proton at position 5. (In the compound 2-methylthiazole the H<sub>5</sub> signal appears somewhat broader due to an unresolved coupling arising from the methyl group at position 2.) Protons H<sub>2</sub> and H<sub>4</sub> are both two bonds removed from the nitrogen atom whereas H<sub>5</sub> is



TABLE I

Proton chemical shifts and spin-coupling constants for thiazole and methylthiazoles

Compound	Chemical shifts* (cycles/sec)			Spin-coupling constants (cycles/sec)		
	H <sub>2</sub>	H <sub>4</sub>	H <sub>5</sub>	J <sub>24</sub>	J <sub>45</sub>	J <sub>25</sub>
Thiazole	-231	-170	-135	0	3.1	1.8
2-Methylthiazole	—	-152	-125	—	3.6	—
4-Methylthiazole	-220	—	-107	—	—	2.0
2,4-Dimethylthiazole	—	—	-94	—	—	—

\*Measured at 60 Mc/s, in cycles per second relative to proton resonance of water (external reference).

three bonds removed. It is evident that the H<sub>2</sub> and H<sub>4</sub> signals are broadened by the nitrogen quadrupole relaxation and that this perturbation becomes sufficiently attenuated at proton H<sub>5</sub> to give rise to more nearly normal proton line widths. A similar behavior is observable in the proton resonance spectrum of pyridine, the proton signals of the  $\alpha$ -hydrogens being noticeably broader than those of the  $\beta$ -hydrogens. In both thiazole and pyridine the electronic charge distribution about the nitrogen atom can be concluded to be highly asymmetric.

The electronegativity of C and S atoms is generally considered to be comparable and significantly less than that of the N atom (4). Thus the signals of H<sub>2</sub> and H<sub>4</sub> may be expected to appear at lower field than that of H<sub>5</sub>, but the reason for the large difference in chemical shift between H<sub>2</sub> and H<sub>4</sub> is not readily apparent. The signal of proton H<sub>2</sub>, which is in the  $\alpha$ -position with respect to both S and N atoms, appears at considerably lower field than that of H<sub>4</sub>, which is in the  $\alpha$ -position with respect to C and N atoms. It may be noted further that methyl substitution in all cases shifts the ring proton signals to higher field, suggesting a high degree of "aromaticity" in the ring.

A further anomaly is to be found in the spin-coupling constants. Thus the proton pairs H<sub>2</sub> and H<sub>4</sub> and H<sub>2</sub> and H<sub>5</sub> are separated by an equal number of bonds between them, but while J<sub>25</sub> is of the order of 2.0 cycles/sec, J<sub>24</sub> could not be resolved. The possibility that the spin coupling between H<sub>2</sub> and H<sub>4</sub>, which must go via the N atom, is perturbed by the nitrogen quadrupole relaxation must be considered. Since the coupling between H<sub>2</sub> and H<sub>5</sub> is via the S atom, which is a non-magnetic nucleus, this coupling is unperturbed. The coupling between H<sub>2</sub> and H<sub>4</sub> can of course also proceed via the S atom, but since this path involves an additional bond the coupling will be significantly less.

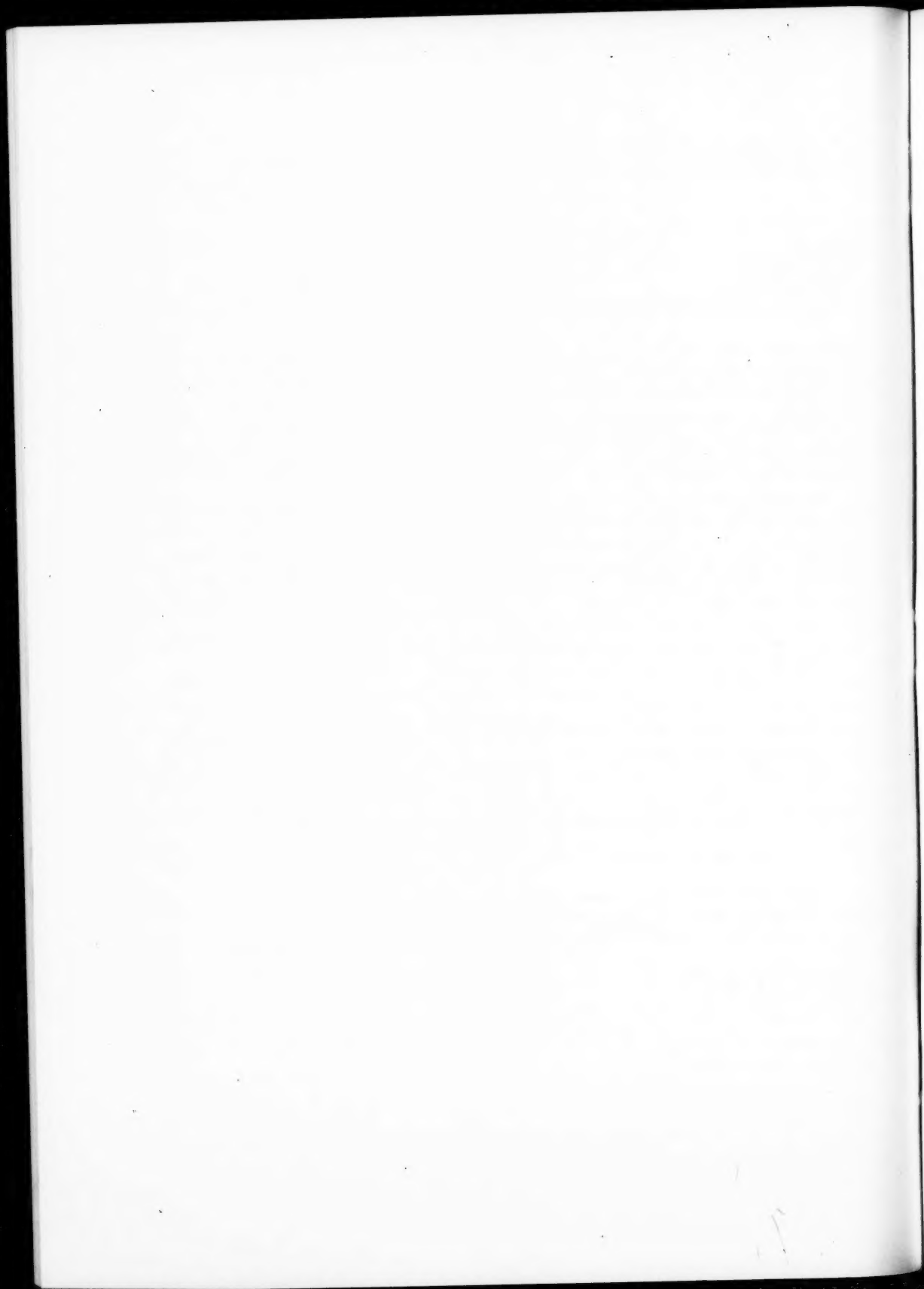
The authors wish to thank Mr. J. Nicholson for technical assistance.

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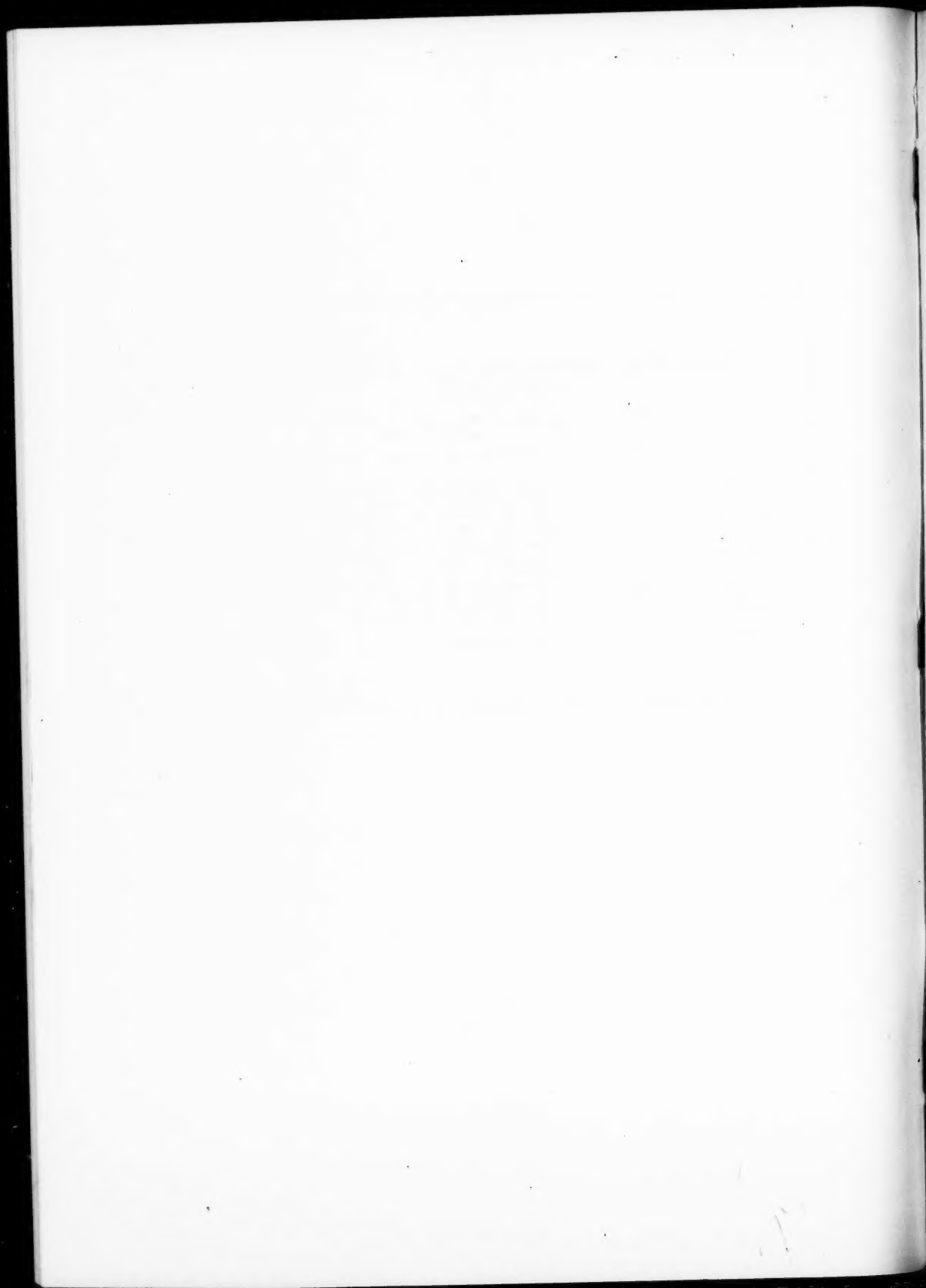
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